

# PATENT ABSTRACTS OF JAPAN

(11)Publication number : 11-115308

(43)Date of publication of application : 27.04.1999

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(51)Int.CI.

B41M 5/00  
B41J 2/01

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(21)Application number : 09-296285

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(22)Date of filing : 14.10.1997

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## (54) RECORDING SHEET

### (57)Abstract:

**PROBLEM TO BE SOLVED:** To provide the recording sheet having a colorant accepting layer, which can obtain an image sheet through ink jet recording, thermal transfer recording or electrophotographic recording and at the application and drying of which no crack develops and which can easily be formed.

**SOLUTION:** In a recording sheet, in which a colorant accepting layer is provided on a support, the colorant accepting layer is formed by applying a coating fluid including fine inorganic particles and a water-soluble resin onto the support. By giving a solution including a crosslinker, which can crosslink the water-soluble resin simultaneously with the coating the coating fluid or during a period, in which a coated layer shows a constant rate drying speed, (or before the arrival of a falling rate drying speed), through a method such as coating or the like to the coated layer for hardening in order to the recording sheet.

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## LEGAL STATUS

[Date of request for examination] 14.10.2003

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

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CLAIMS

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[Claim(s)]

[Claim 1] The sheet for record characterized by to be the layer obtained by this color-material acceptance layer applying the coating liquid containing a non-subtlety particle and water soluble resin on a base material in the sheet for record with which it comes to prepare a color-material acceptance layer on a base material, giving the solution which contains the cross linking agent over which this water soluble resin can be made to construct a bridge this spreading, coincidence, or before the applied this layer comes to show the falling rate of drying, and making it harden.

[Claim 2] The sheet for record according to claim 1 whose cross linking agent is boric acid or borate.

[Claim 3] The sheet for record according to claim 1 or 2 whose primary [ an average of ] particle diameter a non-subtlety particle is a silica particle 20nm or less.

[Claim 4] The sheet for record according to claim 1 to 3 whose water soluble resin is polyvinyl alcohol.

[Claim 5] The sheet for record according to claim 1 to 4 which has the weight ratio of a non-subtlety particle and water soluble resin in the range of 1.5:1-10:1.

[Claim 6] The sheet for record according to claim 1 to 5 with which the above-mentioned color-material acceptance layer has 40 – 80% of voidage.

[Claim 7] The sheet for record according to claim 1 to 6 with which the above-mentioned color-material acceptance layer contains the silane coupling agent which has a basic group.

[Claim 8] The sheet for record according to claim 1 to 7 which is the layer obtained by carrying out simultaneous spreading and stiffening further this cross linking agent and the liquid which does not react so that the layer of the liquid may intervene between the layer of coating liquid, and the layer of the solution of a cross linking agent in case this color-material acceptance layer carries out simultaneous spreading of the coating liquid containing a non-subtlety particle and water soluble resin, and the solution of this cross linking agent.

[Claim 9] The sheet for record according to claim 1 to 8 which is an object for ink jet record.

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

#### [0001]

[Industrial Application] This invention relates to the record sheet recorded using color material. In order to form an image sheet by ink jet record, thermal transfer recording, electrophotography record, etc. especially, it is related with the record sheet used advantageously.

#### [0002]

[Description of the Prior Art] In recent years, the record approach and equipment which various information processing system was developed and fitted each information system are also developed and adopted with rapid development of an information industry. It miniaturizes with lightweight-ization, and the noise does not have equipment used in such a record approach in the thermal-ink-transfer-printing record using the ink record using an ink jet or a plotter and melting mold color material, or sublimation mold color material, either, and it has become the thing excellent also in operability and maintainability. Furthermore, the equipment used by such record approach is widely used from colorization being easy recently. Moreover, colorization progresses also in the conventional electrophotography method, and a full color printer and a full color copying machine have been developed and commercialized with high resolution.

[0003] although the method of various kinds [ method / ink jet ] is developed — an object — there are three sorts, the approach using the coloring matter solution (water color ink) which roughly divides sexually and contains water-soluble coloring matter, the approach using the coloring matter solution (oily ink) containing oil solubility coloring matter, and the method of carrying out thermofusion of the low melting point solid wax (wax ink) containing coloring matter, and using it. The mainstream is a type which uses water color ink. Anyway, it is the approach of making the front face of an ink record sheet breathe out a liquefied particle drop, and forming an image in it.

[0004] A thermal-ink-transfer-printing method is roughly divided, and has two sorts of methods. The 1st method is the approach (heat-of-fusion imprint) of making a record sheet imprinting and obtaining an image, by carrying out melting to the shape of a pattern which carried out heat impression of the ink of the thermofusion nature by which coating was carried out on the base material by heat impression from a base material side. The 2nd method is the approach (heat-of-sublimation imprint) of making a record sheet imprinting and obtaining an image, by performing heat impression from a base material side into the thermal recording ingredient which consists of the resin and the sublimability color of high softening temperature on a base material like the former, and making a sublimation color sublimate to it in the shape of [ which carried out heat impression ] a pattern. An electrophotography method has the approach in use of giving an optical image pattern to the electrified photoconduction layer, forming an electrostatic latent image, imprinting after toner development subsequently to a record sheet, and carrying out melting fixation of the toner with heat.

[0005] On the other hand, it is necessary to use a transparency sheet, and for the following applications, using the bright film which prepared the color-material acceptance (absorption) layer in the front face, image formation of many is carried out as mentioned above, and they create a record sheet. For example, the OHP film whose opportunity used instead of a slide at a board etc. is increasing, the film for a back light display whose opportunity used instead of a printing poster or

a display board is increasing, the film for mother prints, etc. can be mentioned.

[0006] The bright film in which the image was formed by the above-mentioned recording method requires that color material should have pasted up firmly on the surface of a record sheet in addition to the hue of the image obtained, saturation, and lightness, and further, in the case of ink jet record, when obtaining a minute image, liquefied ink is absorbed early, and it is required that there is neither an ink blot nor ink \*\*\*\*\* etc.

[0007] In order to solve these troubles, various proposals are made from the former. For example, the sheet for record which becomes JP,57-14091,A and JP,61-19389,A from the clear layer of a transparency base material, and the colloidal silica and water soluble resin which were prepared on it is proposed. However, as for this clear layer, since the particle of colloidal silica is too large and there are too many amounts of water soluble resin, voidage big enough is not obtained, but for this reason, the above-mentioned sheet for record has the problem that ink rate of absorption large enough is hard to be shown.

[0008] Moreover, the sheet for record possessing the color-material acceptance layer which has the pore formed from the pseudo-boehmite particle is indicated by JP,2-276670,A and JP,3-281383,A. According to examination of this invention person, although ink absorptivity of this sheet for record improved, since the refractive index was as high as 1.65, it became clear that transparency high enough was not acquired.

[0009] The sheet for record which has the clear layer which becomes JP,61-53598,A from a base material, and the particle and water soluble resin of a synthetic silica and refractive indexes 1.44-1.55 which were prepared on it further again is indicated. A synthetic silica has a diameter of a primary particle usually exceeding 10nm, and an aggregated particle serves as particle size of several 100nm further. The sheet for record containing such a particle does not show light transmission high enough that such aggregated particles tend to be scattered [ therefore ] about in light. Furthermore, since a clear layer is a big aggregated particle and it has a ratio and many [ \*\*-wise ] holes, generating of an ink blot or ink \*\*\*\*\* cannot fully be prevented.

[0010] The sheet for record with which the color-material acceptance layer which has the three-dimensional structure of the high voidage formed in JP,7-276789,A from a non-subtlety particle and water soluble resin as a sheet for record which solved the above-mentioned problem was prepared on the transparency base material is proposed. Control of the above-mentioned ink absorptivity and a color mixture blot is presupposed by this configuration that it is enough and an image with high resolution can be obtained.

[0011]

[Problem(s) to be Solved by the Invention] Generally, the high color-material acceptance layer of voidage formed from a non-subtlety particle and water soluble resin has a small particle, and it is [ the content of a particle ] large. And when the coating liquid containing the ingredient for forming such a color-material acceptance layer was applied, while drying the spreading layer, it became clear by examination of this invention person that a cracking crack may occur. And especially this cracking crack became clear [ that it is easy to generate when it dries at comparatively high temperature ], in order to shorten the drying time. Although the approach of making viscosity of the binder of coating liquid comparatively high is proposed by JP,9-109545,A as an approach of preventing this cracking crack, since it is easy to generate spreading nonuniformity etc. and leads to lowering of workability by this approach, it is not desirable. Moreover, this approach cannot be said to be enough in the cracking crack prevention effectiveness.

[0012] In order to prevent the cracking crack of the above-mentioned color-material acceptance layer, when this invention person repeated examination, the cracking crack of a spreading layer became clear [ generating at the stage shifting to decreasing drying ] in the middle of the desiccation (i.e., constant rate drying), after applying the coating liquid for color-material acceptance stratification on the base material. In the condition of the constant rate drying before this invention person repeats examination further and a decreasing drying condition starts based on this knowledge, by raising the film reinforcement of a spreading layer as early as possible, it found out that a cracking crack could be prevented and this invention was reached.

[0013] Therefore, this invention aims at being able to obtain an image sheet by ink jet record, thermal transfer recording, or electrophotography record, and offering the sheet for the record

which has the color-material acceptance layer which a cracking crack cannot generate easily at the time of spreading desiccation, and can be formed simply.

[0014] Especially this invention aims at offering the sheet for record suitable for the ink jet record which has the color-material acceptance layer which can be formed simply, without absorbing liquefied ink promptly, and there being no absorption nonuniformity of ink, and being able to obtain a minute image without an ink blot or ink \*\*\*\*\*\*, and a cracking crack occurring at the time of spreading desiccation.

[0015]

[Means for Solving the Problem] In the sheet for record with which, as for this invention, it comes to prepare a color-material acceptance layer on a base material This color-material acceptance layer applies the coating liquid containing a non-subtlety particle and water soluble resin on a base material. This spreading, coincidence, or before the applied this layer comes to show the falling rate of drying, it is in the sheet for record characterized by being the layer obtained by giving and stiffening the solution containing the cross linking agent over which this water soluble resin can be made to construct a bridge.

[0016] The desirable mode of the sheet for record of above-mentioned this invention is as follows.

(1) A cross linking agent is boric acid or borate.

(2) A non-subtlety particle is [ primary / an average of / particle diameter ] a silica particle 20nm or less (preferably 10nm or less, especially the range of 3–10nm).

(3) Water soluble resin is polyvinyl alcohol or gelatin.

(4) The weight ratio of a non-subtlety particle and water soluble resin is in the range of 1.5:1–10:1.

(5) A color-material acceptance layer has 40 – 80% of voidage (especially 50 – 80% of voidage).

[0017] (6) In case (7) color-material acceptance layer in which a color-material acceptance layer contains the silane coupling agent which has a basic group (especially quaternary ammonium base) carries out simultaneous spreading of the coating liquid containing a non-subtlety particle and water soluble resin, and the solution of this cross linking agent, it is the layer obtained by carrying out simultaneous spreading and stiffening further this cross linking agent and the liquid which does not react so that the layer of the liquid may intervene between the layer of coating liquid, and the layer of the solution of a cross linking agent.

(8) The sheet for record is an object for ink jet record.

[0018] (9) The coverage on the color-material acceptance layer of a cross linking agent content solution is 0.01–10g/m<sup>2</sup> by cross linking agent conversion. It is in the range (the range of 0.05 – 5 g/m<sup>2</sup>).

(10) A color-material acceptance layer has a three-dimensional network.

(11) A color-material acceptance layer has 30% or less of Hayes.

(12) The above-mentioned sheet for record for ink jet record whose thickness of a color-material acceptance layer is 10–50 micrometers.

(13) The object for electrophotography or the sheet for the above-mentioned record for thermal recording whose thickness of a color-material acceptance layer is 0.1–10 micrometers.

[0019]

[Embodiment of the Invention] The sheet for record of this invention has the basic configuration which consists of a base material and a color-material acceptance layer formed on the base material, for example, can manufacture it as follows.

[0020] Opaque ingredients, such as paper, may be used, using transparent materials, such as plastics, as an ingredient which can be used as the above-mentioned base material. When employing the transparency of a color-material acceptance layer efficiently in this invention, as for a base material, it is desirable that they are a transparency base material or the opaque base material of high gloss. As an ingredient which can be used as a transparency base material, it is transparent and the ingredient which has the property to bear the radiant heat when being used on OHP or a back light display is desirable. As such an ingredient, cellulose ester, such as polyester, nitrocelluloses, such as polyethylene terephthalate, cellulose acetate, and cellulose acetate butylate, and polysulfone, polyphenylene oxide, polyimide, a polycarbonate, a polyamide, etc. can be mentioned. Polyester is desirable in these and especially polyethylene phthalate is desirable. Its thickness of a transparency base material is easy to deal with a 50–200-micrometer thing and is

desirable although there is especially no limit.

[0021] That in which the near front face in which a color-material acceptance layer is prepared has 40% or more of glossiness as an opaque base material of high gloss is desirable. The above-mentioned glossiness is JIS. It is the value calculated by measuring according to the approach of a publication to P-8142 (75-degree specular gloss test method of paper and the paper board). As an example of the opaque base material of high gloss, art paper, coat paper, a cast-coated paper, Paper of high gloss, such as a baryta paper used for the base material for film photos etc.; Polyester, such as polyethylene terephthalate (PET) Cellulose ester, such as a nitrocellulose, cellulose acetate, and cellulose acetate butylate With or plastic films, such as polysulfone, polyphenylene oxide, polyimide, a polycarbonate, and a polyamide The film of the high gloss which this film was made to contain white pigments etc. and was made opaque (performing surface calender processing etc.), Or the film with which the enveloping layer of the polyolefine which contains white pigments or is not contained was prepared in the front face of content plastics, such as the various above-mentioned papers, the above-mentioned transparency plastic film, or white pigments, can be mentioned. Furthermore, white-pigments content foaming polyester film (calcium content foaming PET which was made to contain an example and a polyolefine particle and formed the opening by drawing) can also be mentioned. Moreover, the special kind paper in which the polyolefine coat paper (a kind of the base material with which the enveloping layer of polyolefines, such as a paper base material with which the white-pigments content polyolefine layer was prepared in the front face, was prepared) currently generally used as a base material for film photos, or a metal vacuum evaporationo layer was prepared can be used suitably. The paper base material with which the white-pigments content polyolefine layer was prepared especially, the polyester (preferably PET) film with which the white-pigments content polyolefine layer was prepared, white-pigments content polyester film, or white-pigments content foaming polyester film is desirable. Its thickness of an opaque base material is easy to deal with a 50–200-micrometer thing and is desirable although there is especially no limit.

[0022] Moreover, a base material may use what performed corona discharge treatment, flame treatment, and UV irradiation processing.

[0023] In case the color-material acceptance layer of this invention applies the coating liquid containing a non-subtlety particle and water soluble resin on a base material, this spreading, coincidence, or before the applied this layer comes to show the falling rate of drying, it is a layer which the water soluble resin obtained by giving and stiffening the solution of a cross linking agent on a spreading layer hardened by the cross linking agent.

[0024] As an example of water soluble resin, it is resin which has hydroxyl as a hydrophilic structural unit, polyvinyl alcohol (PVA) and cellulose type resin (methyl cellulose (MC) —) Ethyl cellulose (EC), hydroxyethyl cellulose (HEC), Chitins and starches, such as a carboxymethyl cellulose (CMC); The polyethylene oxide which is resin which has ether linkage (PEO), The polyacrylamide (PAAM) and the polyvinyl pyrrolidone (PVP) which are resin which has polypropylene oxide (PPO), polyethylene-glycol (PEG), and polyvinyl ether (PVE); an amide group, and amide association can be mentioned. Moreover, the polyacrylate which has a carboxyl group as a dissociative radical, maleic resin, alginate, and gelatin; the poly allylamine (PAA) which has the polystyrene sulfonate salt which has a sulfone radical, the amino group, an imino group, the 3rd amine, and quarternary ammonium salt, polyethyleneimine (PEI), an epoxidation polyamide (EPAm), polyvinyl pyridine, and gelatin can be mentioned.

[0025] As a non-subtlety particle, a silica particle, colloidal silica, a calcium silicate, a zeolite, a kaolinite, halloysite, a muscovite, talc, a calcium carbonate, a calcium sulfate, boehmite, pseudo-boehmite, etc. can be mentioned, for example. What has a refractive index in the range of 1.40–1.60 from the point of not reducing transparency is desirable. A silica particle is desirable in these.

Moreover, the first [ an average of ] particle diameter of a non-subtlety particle has common 20nm or less (preferably 10nm or less, especially 3–10nm), and, as for a refractive index, it is desirable that they are the 1.45 neighborhoods.

[0026] By the hydrogen bond by the surface silanol group, for an adhesion and cone reason, particles can form the structure where especially voidage is large, when especially the first [ an average of ] particle diameter is 10nm or less as mentioned above, and the ink absorption property

of a silica particle improves. A silica particle is divided roughly into a wet method and dry process according to a manufacturing method. The method of the acidolysis of a silicate generating active silica, carrying out the polymerization of this moderately in a wet method, carrying out flocking settling, and obtaining a water silica is in use. One dry-process silica has a method in use of obtaining an anhydrous silica by the approach (arc process) of carrying out heating hydride generation of the approach (flame hydrolysis), silica sand, and corks by elevated-temperature gaseous-phase hydrolysis of silicon halide with an arc in an electric furnace, and oxidizing this with air. In the case of a silicic anhydride (anhydrous silica), especially voidage is easy to form the high three-dimensional structure and is desirable [ a silica ], although these water silicas and an anhydrous silica have a difference in the consistency of a surface silanol group, the existence of a hole, etc. and show a property different, respectively. This reason is 2 5-8 pieces/nm, when the consistency of a surface silanol group is a water silica, although it is not clear. Mostly, when it is easy to condense a particle densely (aggregate) and it is one anhydrous silica, it is 2 2-3 pieces/nm. Since it is few, it is presumed that it is because it becomes \*\*\*\* flocculation (FUROKYU rate) and voidage becomes high structure.

[0027] The class of resin combined with a silica particle from a viewpoint of transparency is important, and when it is an anhydrous silica, PVA, especially PVA of whenever [ low saponification ] (70 – 90% whenever [ saponification ] it is desirable) are suitable in respect of light transmission nature. Although PVA has a hydroxyl group in a structural unit, they make easy for this hydroxyl group and the silanol group of a silica particle front face to form hydrogen bond, and to form the three-dimensional network which makes the aggregated particle of a silica particle a chain unit, and it is thought that the color-material acceptance layer of the structure where voidage is high is obtained by this. Thus, not only the minute record which absorbs ink quickly by capillarity and has neither an ink blot nor ink \*\*\*\*\* is possible, but the obtained porous layer can paste up firmly the color material in thermal recording, and the toner in electrophotography record in ink jet record. This reason is because color material and a toner go underwater in the pore of a porous layer, the geometrical anchor effect which originates in a three-dimensional network as that result occurs and this fixes color material etc. firmly. Moreover, since there are many rates of a non-subtlety particle, thermal resistance is high and the embossing-proof nature in electrophotography record also has the description of being high.

[0028] The ratio (PB ratio: weight of the non-subtlety particle to the weight 1 of water soluble resin) of a non-subtlety particle (preferably silica particle) and water soluble resin has big effect also on membrane structure. If PB ratio becomes large, voidage, pore volume, and surface area (per unit weight) will become large. When a ratio exceeds 10, there is no effectiveness over film reinforcement and the cracking crack at the time of desiccation, less than by 1.5, an opening is closed by resin, voidage decreases and ink absorptivity ability falls. For this reason, the range of 1.5-10 is suitable for PB ratio. Like especially an OHP film, in order to acquire high-speed ink absorptivity with an ink jet printer, as for especially PB ratio, two or more are desirable [ to touch the image of a record sheet directly by hand, it is necessary to obtain sufficient film reinforcement, as for especially PB ratio, five or less are desirable, and ], therefore the range of 2-5 is still more suitable for PB ratio.

[0029] For example, the three-dimensional network which makes the aggregated particle of a silica particle a chain unit when the first [ an average of ] above particle diameter distributes thoroughly [ PB ratio / 2-5 ] in a water solution an anhydrous silica and water soluble resin 10nm or less and carries out spreading desiccation is formed, average pore is 30nm or less, and voidage is 50% or more and pore specific volume 0.5 ml/g. The above and specific surface area are 100m<sup>2</sup>/g. The porous membrane of the above translucency can be formed easily.

[0030] The color-material acceptance layer of this invention is a layer which hardened further the layer (porous layer) which uses the above-mentioned inorganic particle and water soluble resin as a principal component by the cross linking agent. And in this invention, grant of a cross linking agent is performed, at the same time the above-mentioned coating liquid for porous layer formation was applied, or before the coating liquid layer for porous layer formation comes to show the falling rate of drying. The cracking crack generated by this actuation while the spreading layer of the coating liquid for porous layer formation dries can be prevented. That is, before a spreading layer comes to

show the falling rate of drying at the same time the above-mentioned coating liquid for porous layer formation was applied or, the given cross linking agent content solution raises the film reinforcement of a spreading layer substantially immediately by permeating in a spreading layer, reacting promptly with the water soluble resin in a spreading layer, and making water soluble resin macromolecule-ize (hardening). Consequently, the cracking crack generated at the time of desiccation of the spreading layer of the above-mentioned coating liquid for porous layer formation can be prevented.

[0031] as the example of the cross linking agent to be used — boric acid and borate (an example, an orthoboric salt, and InBO<sub>3</sub> —) ScBO<sub>3</sub>, YBO<sub>3</sub>, LaBO<sub>3</sub>, and Mg<sub>3</sub>(BO<sub>3</sub>)<sub>2</sub>, Co<sub>3</sub>(BO<sub>3</sub>)<sub>2</sub>, diborate (an example, Mg<sub>2</sub>B—O<sub>5</sub>, Co<sub>2</sub>B—O<sub>5</sub>), a metaboric acid salt (an example, LiBO<sub>2</sub>, calcium (BO<sub>2</sub>)<sub>2</sub>, and NaBO<sub>2</sub> —) KBO<sub>2</sub> and tetraborate (example and Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> and 10H<sub>2</sub>O) 5 borate (example, KB<sub>5</sub>O<sub>8</sub>.4H<sub>2</sub>O, and calcium<sub>2</sub>B<sub>6</sub>O<sub>11</sub> and 7H<sub>2</sub>O —) CsB 5O<sub>5</sub>, glyoxal, melamine formaldehyde (an example, a methylol melamine, alkylation methylol melamine), a methylolurea, resol resin, the poly isocyanate, etc. can be mentioned. In these, boric acid or borate is desirable. Since using it combining polyvinyl alcohol as water soluble resin causes crosslinking reaction promptly, boric acid and borate have it. [desirable]

[0032] When using gelatin as water soluble resin, the following compound known as a hardening agent of gelatin can be used as a cross linking agent. Aldehyde system compounds, such as formaldehyde, glyoxal, and a glutaraldehyde; Diacetyl, Ketone system compounds, such as cyclopentane dione; screw (2-chloro ethylurea)-2-hydroxy - 4, 6-dichloro - 1, 3, 5 triazine, Activity halogenated compounds, such as 2 and 4-dichloro-6-S-triazine sodium salt; A divinyl sulfonic acid, A 1, 3-vinyl sulfonyl-2-propanol, N, and N'-ethylene screw (vinyl sulfonyl acetamido), Activity vinyl compounds, such as 1, 3, and 5-thoria chestnut roil-hexahydro-S-triazine; A dimethylolurea, N-methylol compounds, such as methylol dimethylhydantoin; Isocyanate system compound; U.S. Pat. No. 3017280, such as 1 and 6-hexamethylene di-isocyanate, Epoxy system compounds, such as carboxy imide system compound; glycerol triglycidyl ether indicated by aziridine system compound; U.S. Pat. No. 3100704 indicated by 2983611; 1, 6-hexamethylene-N, ethylene imino \*\*\*\*\*; such as an N'-bis-ethylene urea, — halogenation carboxy aldehyde system compound [, such as a mucochloric acid muco phenoxy KURORU acid, ]; — dioxane system compound; chromium alum, such as 2 and 3-dihydroxy dioxane, potash alum, a sulfuric-acid zirconium, chromium acetate, etc. Two or more sorts of these can be combined, and can also be used.

[0033] The solution of the above-mentioned cross linking agent dissolves a cross linking agent in water and/or an organic solvent, and is prepared. The concentration of a cross linking agent solution has 0.05 – 10 desirable % of the weight, and it is 0.1 – 7 % of the weight especially. Generally as a solvent of a cross linking agent, water is used. Halogenation solvents [, such as alcoholic; methyl ethyl ketone, /, such as ketone; ethyl acetate, /, such as ester; toluene, /, such as the ether such as an aromatic series solvent; tetrahydrofuran, and dichloromethane, ], such as a methanol and isopropyl alcohol, etc. can be mentioned that what is necessary is just to use what each ingredient dissolves as an organic solvent.

[0034] In this invention, when the coating liquid (coating liquid for porous layer formation) which uses a non-subtlety particle and water soluble resin as a principal component is applied on a base material, a cross linking agent is given so that this spreading layer may not cause a cracking crack, and the film reinforcement of a spreading layer is raised promptly. After applying the coating liquid which applies a cross linking agent solution to spreading and coincidence of coating liquid which use a non-subtlety particle and solubility resin as a principal component actually, or uses a non-subtlety particle and water soluble resin as a principal component, a cross linking agent solution is given promptly.

[0035] Next, after applying the coating liquid (coating liquid for porous layer formation) which uses a non-subtlety particle and water soluble resin as a principal component, before the spreading layer comes to show the falling rate of drying, how to give a cross linking agent solution promptly is explained. the coating liquid for porous layer formation — an average of 1 [for example,] — the silica particle not more than order particle diameter 10nm — underwater — adding (an example —) A high-speed revolution wet colloid mill (an example, KUREA mix (M Technique Co., Ltd. make)) is used ten to 15% of the weight. For example, after carrying out distribution for 20 minutes

(preferably for 10 – 30 minutes) on condition that the high-speed revolution of 10000rpm (preferably 5000 – 20000rpm), A polyvinyl alcohol water solution (it is set to PVA of about 1/3 weight of an example and a silica like) can be added, and it can obtain by distributing on the still more nearly same conditions as the above. Thus, the obtained coating liquid is a homogeneity sol and can obtain the porous layer which has a three-dimensional network by forming this on a base material by the following method of application.

[0036] Spreading of the above-mentioned coating liquid for porous layer formation can be carried out by applying the coating liquid which added the antistatic agent, the mordant, etc. to for example, the above-mentioned coating liquid further by request, and was obtained on the above-mentioned base material (film). Spreading can be performed by the well-known methods of application, such as for example, an extrusion die coating machine, the Ayr doctor coating machine, a bread coating machine, a rod coating machine, a knife coating machine, a squeeze coating machine, a reverse roll coater, and a bar coating machine.

[0037] After spreading of the coating liquid for porous layer formation, before the spreading layer comes to show the falling rate of drying, the solution containing the cross linking agent of this invention is applied on a spreading layer by the same approach as the above-mentioned coating liquid for porous layer formation, it dries and the color-material acceptance layer by which this invention was hardened is obtained. In addition, a cross linking agent solution may be given by the approach of a spray etc.

[0038] Before the above-mentioned spreading layer comes to show the falling rate of drying, the constant rate of drying which is for several minutes after immediately after spreading, and is the phenomenon in which the content of the solvent in a spreading layer decreases in proportion to time amount in the meantime is usually shown. The period which shows such the constant rate of drying is indicated by the chemical engineering handbook (707–712 pages, the Maruzen Co., Ltd. issuance, October 25, Showa 55).

[0039] After spreading of the coating liquid for porous layer formation, the color-material acceptance layer of this invention gives the above-mentioned cross linking agent content solution by the approach of spreading or a spray, while this spreading layer shows the constant rate of drying. Generally desiccation after spreading of the coating liquid for porous layer formation is performed at 50–180 degrees C for 0.5 – 10 minutes (especially for 0.5 – 5 minutes). Although this drying time naturally changes with coverage, the above-mentioned range is suitable for it.

[0040] Introductory \*\*\*\* of the cross linking agent is carried out into this spreading layer that the spreading layer is immersed in the spreading layer of the coating liquid for porous layer formation in the base material which has this spreading layer in a cross linking agent content solution within the period which shows the constant rate of drying, or by carrying out spray spreading of the cross linking agent content solution at a spreading layer. Although spreading of cross linking agent content coating liquid can use the well-known methods of application, such as a curtain flow coater besides the above-mentioned approach, an extrusion die coating machine, the Ayr doctor coating machine, a bread coating machine, a rod coating machine, a knife coating machine, a squeeze coating machine, a reverse roll coater, and a bar coating machine, its approach a coating machine does not contact a spreading layer directly using an extrusion DAI coating machine, a curtain flow coater, a bar coating machine, etc. is desirable.

[0041] The coverage on the color-material acceptance layer of cross linking agent content coating liquid is 0.01 – 10 g/m<sup>2</sup> by cross linking agent conversion. The range is common and it is 0.05–5g/m<sup>2</sup>. The range is desirable. After spreading of cross linking agent content coating liquid, generally a spreading layer is heated for 0.5 – 30 minutes at 40–180 degrees C, and desiccation and hardening are performed. It is desirable to heat in 1 – 20 minutes at 40–150 degrees C. For example, when using boric acid as a cross linking agent, it is desirable to heat for 5 – 20 minutes at 60–100 degrees C.

[0042] Next, how to apply a cross linking agent solution to spreading and coincidence of the coating liquid (coating liquid for porous layer formation) which uses as a principal component the non-subtlety particle and water soluble resin which are the another formation approach of the color-material acceptance layer of this invention is explained. It can obtain by carrying out simultaneous spreading and stiffening the coating liquid for porous layer formation, and a cross

linking agent content solution on a base material, so that the coating liquid for porous layer formation may contact a base material. Simultaneous spreading of the coating liquid for porous layer formation and a cross linking agent content solution can be performed by the method of application which uses for example, an extrusion DAI coating machine and a curtain flow coater, for example. Generally desiccation after simultaneous spreading (multistory spreading) is performed by heating for 0.5 – 10 minutes at 40–150 degrees C, and a spreading layer is hardened. It is desirable to heat for 0.5 – 5 minutes at further 40–100 degrees C. For example, when using boric acid as a cross linking agent, it is desirable to heat for 5 – 20 minutes at 60–100 degrees C.

[0043] When the above-mentioned multistory spreading is performed for example, by the extrusion die coating machine, multistory is formed before two sorts of coating liquid moves on an extrusion die coating machine, i.e., a base material. And since crosslinking reaction has already occurred by the interface of a bilayer in case the spreading layer (multistory) of a bilayer moves to a base material, it becomes easy to generate thickening by mixing of regurgitation coating liquid near the delivery of an extrusion die coating machine, and trouble may be caused to spreading actuation. Therefore, in case the above-mentioned simultaneous spreading is performed, it is desirable to apply further, a cross linking agent and the liquid which does not react three layers of coincidence with spreading of the coating liquid for porous layer formation and this cross linking agent content solution, so that a layer may be intervened between the layer of coating liquid and the layer of a solution. As a cross linking agent and liquid which does not react, a minute amount \*\*\*\* water solution can be mentioned for a cross linking agent and the water soluble resin (it is used as a thickener) which does not react, for example.

[0044] Moreover, the obtained color-material acceptance layer can raise surface smooth nature, transparency, and paint film reinforcement after spreading and desiccation by letting between roll nips pass under heating and application of pressure using a super calender, gloss calender, etc. However, decline in voidage needs to perform such processing by setting up few conditions in order to reduce voidage (namely, in order for ink absorptivity to fall).

[0045] In the case of ink jet record, the thickness of the obtained color-material acceptance layer needs to have the absorption capacity which absorbs all drops, and it is necessary to determine this in connection with the voidage of a paint film. For example, the amount of ink is 2 8 nL(s)/mm. If it is the case where voidage is 60%, film about 15 micrometers or more is needed for thickness. In ink jet record, the thickness of the range of 10–50 micrometers is desirable. In the case of thermal ink transfer printing or an electrophotography method, since color material or a toner is adsorbed on a front face, a thin film is enough, and it is desirable. [ of 0.1–10-micrometer thickness ]

[0046] Moreover, a single raw material is sufficient as the non-subtlety particle and water soluble resin which mainly constitute the above-mentioned color-material acceptance layer, respectively, and the mixed stock of two or more raw materials is sufficient as them. moreover, the color-material acceptance layer may contain acid alkali as various kinds of mineral and a PH regulator, in order are alike other than this and to raise the dispersibility of a particle, although it mainly consists of the above-mentioned inorganic particle and water soluble resin. Moreover, various kinds of surfactants for the object which raises spreading fitness and surface quality may be used. In order to control surface frictional electrification and exfoliation electrification, or in order to adjust surface electric resistance in a xerography, the metallic-oxide particle with a surfactant with ion conductivity or electronic conductivity may be included. Moreover, a mordant may be used in order to fix coloring matter in ink jet record and to raise a water resisting property. Moreover, various kinds of mat agents for the object which reduces a surface friction property may be included. Furthermore, various kinds of antioxidants for the object which controls degradation of color material again, and an ultraviolet ray absorbent may be included.

[0047] Moreover, between a color-material acceptance layer and a base material, an adhesive property may be raised or undercoat may be prepared for the object of adjusting electric resistance. Furthermore, a color-material acceptance layer may be prepared in both sides, in order to prepare in one side of a base material and to control curl etc. Moreover, an antireflection film may be prepared, in order to raise light transmission nature to the reverse side or both sides when preparing a color-material acceptance layer only in one side in using by OHP etc.

[0048]

[Example]

[0049] [Example 1]

(1) The presentation of the coating liquid for porous layer (front [ bridge formation ] color-material acceptance layer) formation (all the values of the weight section which shows the loadings of all the following coating liquid express solid content or a nonvolatile matter)

\*\* Anhydrous silica particle (primary [ an average of ] particle diameter : 7nm; 10 weight section surface silanol group : 2-3 pieces/nm 2; refractive index : 1.45;)

Aerosil 300 (product made from Japanese Aerosil)

\*\* Polyvinyl alcohol (it is the 81.8%; 3.3 weight section whenever [ saponification ] polymerization-degree 4000-VA440 (Kuraray Co., Ltd. make))

\*\* ion exchange water the polyvinyl alcohol water solution (what was dissolved in the remainder 62.7 weight section of ion exchange water) after adding in the ion exchange water (73.3 weight sections) of \*\* and distributing the silica particle of 136.0 weight sections \*\* for 20 minutes on condition that 10000rpm using a high-speed revolution wet colloid mill (KUREA mix (M Technique Co., Ltd. make)) — in addition, it distributed on the still more nearly same conditions as the above, and the coating liquid for porous layer formation was obtained.

[0050] An extrusion die coating machine is used for the front face of the laminated paper for the photographic printing papers with a thickness of 200 micrometers for the above-mentioned coating liquid, and it is 200 cc/m<sup>2</sup>. It applied by coverage and dried for 3 minutes at 80 degrees C (3m [/second] wind speed) with hot air drying equipment. The spreading layer showed the constant rate of drying in the meantime. For these 3 minutes, after desiccation, promptly, this spreading layer was made immersed in the boric acid content solution of following (2) for 1 second, and it dried for 10 minutes at 80 degrees C. Thereby, desiccation thickness formed the color-material acceptance layer which is 27 micrometers.

[0051]

(2) Boric acid content solution \*\* boric acid 1 Weight section \*\* surfactant (F-144D, Dainippon Ink & Chemicals, Inc. make) 0.2 weight section \*\* ion exchange water The 98.8 weight sections [0052]

(3) Presentation \*\*M-100C of a silane coupling agent solution which has quarternary ammonium salt (Sumitomo Chemical Co., Ltd. make) 1.6 weight section \*\* Para toluenesulfonic acid (10-% of the weight methanol solution) 1.6 weight sections \*\* silane coupling agent (AZ-6160, Nippon Unicar make) 4.0 weight sections \*\* methanol #3.1 bar coating machine is used for the 32.8 weight sections above-mentioned silane coupling agent solution on the above-mentioned color-material acceptance layer, and it is 2.1g/m<sup>2</sup>. It applies by coverage (solid content) and heats for 5 minutes at 80 degrees C after that. The color-material acceptance layer processed by the silane coupling agent which has quarternary ammonium salt was formed. The sheet for record for ink jets was obtained as mentioned above.

[0053] Except having used the following coating liquid for the coating liquid for [example 2] porous layer (front [ bridge formation ] color-material acceptance layer) formation, like the example 1, formation of a color-material acceptance layer and processing of a silane coupling agent were performed, and the sheet for record for ink jets was obtained.

(1) The presentation of the coating liquid for porous layer (front [ bridge formation ] color-material acceptance layer) formation (all the values of the weight section which shows the loadings of all the following coating liquid express solid content or a nonvolatile matter)

\*\* Dry type silica particle (primary [ an average of ] particle diameter : 7nm; 10 weight section surface silanol group : 2-3 pieces/nm 2; refractive index : 1.45;)

Aerosil 300 (product made from Japanese Aerosil)

\*\* Polyvinyl alcohol (it is the 81.8%; 3.0 weight section whenever [ saponification ] polymerization-degree 4000-VA440 (Kuraray Co., Ltd. make))

\*\* Vinyl pyrrolidone/dimethylaminoethyl The 1.5 weight sections The 4th class salt copolymer of methacrylate (the ruby cut PQ11, BASF Japan, Ltd. make) \*\* ion exchange water The 136.0 weight sections [0054] \*\* Add a silica particle in the ion exchange water (73.3 weight sections) of \*\*, the polyvinyl alcohol water solution (what was dissolved in the remainder 62.7 weight section of ion exchange water) after making it distribute for 20 minutes on condition that 10000rpm using a high-speed revolution wet colloid mill (KUREA mix (M Technique Co., Ltd. make)), and the copolymer of

\*\* — in addition, it distributed on the still more nearly same conditions as the above, subsequently to 8–9 pH was adjusted, and the coating liquid for porous layer formation was obtained.

[0055] In the [example 1 of comparison] example 1, the sheet for record for ink jets was similarly produced except having not applied the boric acid content solution of (2).

[0056] In the [example 2 of comparison] example 2, the sheet for record for ink jets was similarly produced except having not applied the boric acid content solution of (2).

[0057] In the [example 3 of comparison] example 1, the sheet for record for ink jets was similarly produced except having changed the desiccation for 3 minutes into desiccation for 4 minutes at this temperature by 80 degrees C (3m [/second] wind speed) with hot air drying equipment (the spreading layer having shown the falling rate of drying in the meantime).

[0058] About the sheet for record for ink jets obtained above, the ink jet fitness was evaluated by the following measuring methods.

(1) Parallel ray permeability was measured using the Hayes hazemeter (HGM-2DP; Suga Test Instruments Co., Ltd. make), and Hayes was obtained. However, in each example and the example of a comparison, above-mentioned Hayes was measured using the sheet for record which used the polyethylene terephthalate film with a thickness of 100 micrometers instead of the laminated paper for the photographic printing papers as a base material, and was obtained.

[0059] (2) It measured using the voidage mercury porosimeter (pore sizer 9320-PC2, Shimadzu Make), distribution was acquired, and the average was calculated.

(3) About the record sheet obtained the degree of gloss, glossiness was measured according to the approach of a publication to JIS-P -8142 (75-degree specular gloss test method of paper and the paper board).

[0060] (4) With the ink rate-of-absorption ink jet printer (PM-700C; Seiko Epson make), Y (yellow), M (Magenta), C (cyanogen), K (black), B (blue), G (green), and R (red) to the sheet for record carried out solid printing, the contact press of the paper was carried out just behind that (after about 10 seconds), and it judged as follows by the existence of the imprint to the paper of ink.

AA: Ink was not imprinted by paper.

CC: Ink was imprinted by paper.

(5) the sheet for generating profit \*\*\*\* record of a cracking crack was observed visually, and it evaluated as follows according to the existence of the cracking crack generated on the front face, and its magnitude.

AA: The result of the above-mentioned assessment as which the cracking crack of the die length beyond CC:3mm as which the cracking crack of the die length which is BB:1–2mm as which a cracking crack is not regarded is regarded is shown in the following table 1.

[0061]

[A table 1]

Table 1————— . \*\*\*\*\* \*\*[I] \*\* – \*\* \*\*\*\*\* . \*\*\*\* \* .

\*\*\*\*\* The \*\*\*\* method The \*\*\*\* method The \*\*\*\* method \*\*\*\*\* \*\*\* ,-----  
\*\*\*\*\* . \*\*\*\* I forerunner . \*\*\*\* . \*\*\*\* . \*\*\*\*\* . \*\*\*\* [ \*\* . \*\*\*\* . \*\*\*\*\* .  
\*\*\*\* ,-----" \*\*\*\*\* . \*\*\*\* [ \*\* . \*\*\*\* . \*\*\*\* . \*\*\*\* . \*\*\*\*\* . \*\*\*\*\* [ \*\*\*\*\* .  
\*\*\*\* . \*\*\*\* . \*\*\*\*\* . \*\*\*\* [ \*\* . \*\*\*\* . \*\*\*\* . \*\*\*\* . \*\*\*\* ; [0062]

[Effect of the Invention] The sheet for record of this invention absorbs liquefied ink early in ink jet record, and it can form a high-definition image simply, without a minute image without an ink blot or ink \*\*\*\*\* not only can obtaining, but causing generating of a cracking crack for the color-material acceptance layer which is a porous layer. Moreover, since it excels in the absorptivity of the record sheet of this invention, and blot prevention, also in the various recording methods of thermal transfer recording or electrophotography record, the adhesive property of color material or a toner improves. Therefore, it can be said that the sheet for record of this invention is a sheet for record which fitted the various record approaches and was excellent in productivity.

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**TECHNICAL FIELD**

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**[Industrial Application]** This invention relates to the record sheet recorded using color material. In order to form an image sheet by ink jet record, thermal transfer recording, electrophotography record, etc. especially, it is related with the record sheet used advantageously.

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## PRIOR ART

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[Description of the Prior Art] In recent years, the record approach and equipment which various information processing system was developed and fitted each information system are also developed and adopted with rapid development of an information industry. It miniaturizes with lightweight-ization, and the noise does not have equipment used in such a record approach in the thermal-ink-transfer-printing record using the ink record using an ink jet or a plotter and melting mold color material, or sublimation mold color material, either, and it has become the thing excellent also in operability and maintainability. Furthermore, the equipment used by such record approach is widely used from colorization being easy recently. Moreover, colorization progresses also in the conventional electrophotography method, and a full color printer and a full color copying machine have been developed and commercialized with high resolution.

[0003] although the method of various kinds [ method / ink jet ] is developed — an object — there are three sorts, the approach using the coloring matter solution (water color ink) which roughly divides sexually and contains water-soluble coloring matter, the approach using the coloring matter solution (oily ink) containing oil solubility coloring matter, and the method of carrying out thermofusion of the low melting point solid wax (wax ink) containing coloring matter, and using it.

The mainstream is a type which uses water color ink. Anyway, it is the approach of making the front face of an ink record sheet breathe out a liquefied particle drop, and forming an image in it.

[0004] A thermal-ink-transfer-printing method is roughly divided, and has two sorts of methods. The 1st method is the approach (heat-of-fusion imprint) of making a record sheet imprinting and obtaining an image, by carrying out melting to the shape of a pattern which carried out heat impression of the ink of the thermofusion nature by which coating was carried out on the base material by heat impression from a base material side. The 2nd method is the approach (heat-of-sublimation imprint) of making a record sheet imprinting and obtaining an image, by performing heat impression from a base material side into the thermal recording ingredient which consists of the resin and the sublimability color of high softening temperature on a base material like the former, and making a sublimation color sublimate to it in the shape of [ which carried out heat impression ] a pattern. An electrophotography method has the approach in use of giving an optical image pattern to the electrified photoconduction layer, forming an electrostatic latent image, imprinting after toner development subsequently to a record sheet, and carrying out melting fixation of the toner with heat.

[0005] On the other hand, it is necessary to use a transparency sheet, and for the following applications, using the bright film which prepared the color-material acceptance (absorption) layer in the front face, image formation of many is carried out as mentioned above, and they create a record sheet. For example, the OHP film whose opportunity used instead of a slide at a board etc. is increasing, the film for a back light display whose opportunity used instead of a printing poster or a display board is increasing, the film for mother prints, etc. can be mentioned.

[0006] The bright film in which the image was formed by the above-mentioned recording method requires that color material should have pasted up firmly on the surface of a record sheet in addition to the hue of the image obtained, saturation, and lightness, and further, in the case of ink jet record, when obtaining a minute image, liquefied ink is absorbed early, and it is required that there is neither an ink blot nor ink \*\*\*\*\* etc.

[0007] In order to solve these troubles, various proposals are made from the former. For example, the sheet for record which becomes JP,57-14091,A and JP,61-19389,A from the clear layer of a transparency base material, and the colloidal silica and water soluble resin which were prepared on it is proposed. However, as for this clear layer, since the particle of colloidal silica is too large and there are too many amounts of water soluble resin, voidage big enough is not obtained, but for this reason, the above-mentioned sheet for record has the problem that ink rate of absorption large enough is hard to be shown.

[0008] Moreover, the sheet for record possessing the color-material acceptance layer which has the pore formed from the pseudo-boehmite particle is indicated by JP,2-276670,A and JP,3-281383,A. According to examination of this invention person, although ink absorptivity of this sheet for record improved, since the refractive index was as high as 1.65, it became clear that transparency high enough was not acquired.

[0009] The sheet for record which has the clear layer which becomes JP,61-53598,A from a base material, and the particle and water soluble resin of a synthetic silica and refractive indexes 1.44-1.55 which were prepared on it further again is indicated. A synthetic silica has a diameter of a primary particle usually exceeding 10nm, and an aggregated particle serves as particle size of several 100nm further. The sheet for record containing such a particle does not show light transmission high enough that such aggregated particles tend to be scattered [ therefore ] about in light. Furthermore, since a clear layer is a big aggregated particle and it has a ratio and many [ \*\*-wise ] holes, generating of an ink blot or ink \*\*\*\*\* cannot fully be prevented.

[0010] The sheet for record with which the color-material acceptance layer which has the three-dimensional structure of the high voidage formed in JP,7-276789,A from a non-subtlety particle and water soluble resin as a sheet for record which solved the above-mentioned problem was prepared on the transparency base material is proposed. Control of the above-mentioned ink absorptivity and a color mixture blot is presupposed by this configuration that it is enough and an image with high resolution can be obtained.

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## EFFECT OF THE INVENTION

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[Effect of the Invention] The sheet for record of this invention absorbs liquefied ink early in ink jet record, and it can form a high-definition image simply, without a minute image without an ink blot or ink \*\*\*\*\* not only can obtaining, but causing generating of a cracking crack for the color-material acceptance layer which is a porous layer. Moreover, since it excels in the absorptivity of the record sheet of this invention, and blot prevention, also in the various recording methods of thermal transfer recording or electrophotography record, the adhesive property of color material or a toner improves. Therefore, it can be said that the sheet for record of this invention is a sheet for record which fitted the various record approaches and was excellent in productivity.

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## TECHNICAL PROBLEM

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[Problem(s) to be Solved by the Invention] Generally, the high color-material acceptance layer of voidage formed from a non-subtlety particle and water soluble resin has a small particle, and it is [ the content of a particle ] large. And when the coating liquid containing the ingredient for forming such a color-material acceptance layer was applied, while drying the spreading layer, it became clear by examination of this invention person that a cracking crack may occur. And especially this cracking crack became clear [ that it is easy to generate when it dries at comparatively high temperature ], in order to shorten the drying time. Although the approach of making viscosity of the binder of coating liquid comparatively high is proposed by JP,9-109545,A as an approach of preventing this cracking crack, since it is easy to generate spreading nonuniformity etc. and leads to lowering of workability by this approach, it is not desirable. Moreover, this approach cannot be said to be enough in the cracking crack prevention effectiveness.

[0012] In order to prevent the cracking crack of the above-mentioned color-material acceptance layer, when this invention person repeated examination, the cracking crack of a spreading layer became clear [ generating at the stage shifting to decreasing drying ] in the middle of the desiccation (i.e., constant rate drying), after applying the coating liquid for color-material acceptance stratification on the base material. In the condition of the constant rate drying before this invention person repeats examination further and a decreasing drying condition starts based on this knowledge, by raising the film reinforcement of a spreading layer as early as possible, it found out that a cracking crack could be prevented and this invention was reached.

[0013] Therefore, this invention aims at being able to obtain an image sheet by ink jet record, thermal transfer recording, or electrophotography record, and offering the sheet for the record which has the color-material acceptance layer which a cracking crack cannot generate easily at the time of spreading desiccation, and can be formed simply.

[0014] Especially this invention aims at offering the sheet for record suitable for the ink jet record which has the color-material acceptance layer which can be formed simply, without absorbing liquefied ink promptly, and there being no absorption nonuniformity of ink, and being able to obtain a minute image without an ink blot or ink \*\*\*\*\* , and a cracking crack occurring at the time of spreading desiccation.

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## MEANS

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[Means for Solving the Problem] In the sheet for record with which, as for this invention, it comes to prepare a color-material acceptance layer on a base material This color-material acceptance layer applies the coating liquid containing a non-subtlety particle and water soluble resin on a base material. This spreading, coincidence, or before the applied this layer comes to show the falling rate of drying, it is in the sheet for record characterized by being the layer obtained by giving and stiffening the solution containing the cross linking agent over which this water soluble resin can be made to construct a bridge.

[0016] The desirable mode of the sheet for record of above-mentioned this invention is as follows.

- (1) A cross linking agent is boric acid or borate.
- (2) A non-subtlety particle is [ primary / an average of / particle diameter ] a silica particle 20nm or less (preferably 10nm or less, especially the range of 3–10nm).
- (3) Water soluble resin is polyvinyl alcohol or gelatin.

(4) The weight ratio of a non-subtlety particle and water soluble resin is in the range of 1.5:1–10:1.

(5) A color-material acceptance layer has 40 – 80% of voidage (especially 50 – 80% of voidage).

[0017] (6) In case (7) color-material acceptance layer in which a color-material acceptance layer contains the silane coupling agent which has a basic group (especially quaternary ammonium base) carries out simultaneous spreading of the coating liquid containing a non-subtlety particle and water soluble resin, and the solution of this cross linking agent, it is the layer obtained by carrying out simultaneous spreading and stiffening further this cross linking agent and the liquid which does not react so that the layer of the liquid may intervene between the layer of coating liquid, and the layer of the solution of a cross linking agent.

(8) The sheet for record is an object for ink jet record.

[0018] (9) The coverage on the color-material acceptance layer of a cross linking agent content solution is 0.01–10g/m<sup>2</sup> by cross linking agent conversion. It is in the range (the range of 0.05 – 5 g/m<sup>2</sup>).

(10) A color-material acceptance layer has a three-dimensional network.

(11) A color-material acceptance layer has 30% or less of Hayes.

(12) The above-mentioned sheet for record for ink jet record whose thickness of a color-material acceptance layer is 10–50 micrometers.

(13) The object for electrophotography or the sheet for the above-mentioned record for thermal recording whose thickness of a color-material acceptance layer is 0.1–10 micrometers.

[0019]

[Embodiment of the Invention] The sheet for record of this invention has the basic configuration which consists of a base material and a color-material acceptance layer formed on the base material, for example, can manufacture it as follows.

[0020] Opaque ingredients, such as paper, may be used, using transparent materials, such as plastics, as an ingredient which can be used as the above-mentioned base material. When employing the transparency of a color-material acceptance layer efficiently in this invention, as for a base material, it is desirable that they are a transparency base material or the opaque base material of high gloss. As an ingredient which can be used as a transparency base material, it is transparent and the ingredient which has the property to bear the radiant heat when being used on

OHP or a back light display is desirable. As such an ingredient, cellulose ester, such as polyester, nitrocelluloses, such as polyethylene terephthalate, cellulose acetate, and cellulose acetate butylate, and polysulfone, polyphenylene oxide, polyimide, a polycarbonate, a polyamide, etc. can be mentioned. Polyester is desirable in these and especially polyethylene phthalate is desirable. Its thickness of a transparency base material is easy to deal with a 50–200–micrometer thing and is desirable although there is especially no limit.

[0021] That in which the near front face in which a color–material acceptance layer is prepared has 40% or more of glossiness as an opaque base material of high gloss is desirable. The above-mentioned glossiness is JIS. It is the value calculated by measuring according to the approach of a publication to P-8142 (75-degree specular gloss test method of paper and the paper board). As an example of the opaque base material of high gloss, art paper, coat paper, a cast–coated paper, Paper of high gloss, such as a baryta paper used for the base material for film photos etc.; Polyester, such as polyethylene terephthalate (PET) Cellulose ester, such as a nitrocellulose, cellulose acetate, and cellulose acetate butylate With or plastic films, such as polysulfone, polyphenylene oxide, polyimide, a polycarbonate, and a polyamide The film of the high gloss which this film was made to contain white pigments etc. and was made opaque (performing surface calender processing etc.), Or the film with which the enveloping layer of the polyolefine which contains white pigments or is not contained was prepared in the front face of content plastics, such as the various above-mentioned papers, the above-mentioned transparency plastic film, or white pigments, can be mentioned. Furthermore, white–pigments content foaming polyester film (calcium content foaming PET which was made to contain an example and a polyolefine particle and formed the opening by drawing) can also be mentioned. Moreover, the special kind paper in which the polyolefine coat paper (a kind of the base material with which the enveloping layer of polyolefines, such as a paper base material with which the white–pigments content polyolefine layer was prepared in the front face, was prepared) currently generally used as a base material for film photos, or a metal vacuum evaporationo layer was prepared can be used suitably. The paper base material with which the white–pigments content polyolefine layer was prepared especially, the polyester (preferably PET) film with which the white–pigments content polyolefine layer was prepared, white–pigments content polyester film, or white–pigments content foaming polyester film is desirable. Its thickness of an opaque base material is easy to deal with a 50–200–micrometer thing and is desirable although there is especially no limit.

[0022] Moreover, a base material may use what performed corona discharge treatment, flame treatment, and UV irradiation processing.

[0023] In case the color–material acceptance layer of this invention applies the coating liquid containing a non–subtlety particle and water soluble resin on a base material, this spreading, coincidence, or before the applied this layer comes to show the falling rate of drying, it is a layer which the water soluble resin obtained by giving and stiffening the solution of a cross linking agent on a spreading layer hardened by the cross linking agent.

[0024] As an example of water soluble resin, it is resin which has hydroxyl as a hydrophilic structural unit. polyvinyl alcohol (PVA) and cellulose type resin (methyl cellulose (MC) —) Ethyl cellulose (EC), hydroxyethyl cellulose (HEC), Chitins and starches, such as a carboxymethyl cellulose (CMC); The polyethylene oxide which is resin which has ether linkage (PEO), The polyacrylamide (PAAM) and the polyvinyl pyrrolidone (PVP) which are resin which has polypropylene oxide (PPO), polyethylene–glycol (PEG), and polyvinyl ether (PVE);, an amide group, and amide association can be mentioned. Moreover, the polyacrylate which has a carboxyl group as a dissociative radical, maleic resin, alginate, and gelatin; the poly allylamine (PAA) which has the polystyrene sulfonate salt which has a sulfone radical, the amino group, an imino group, the 3rd amine, and quaternary ammonium salt, polyethyleneimine (PEI), an epoxidation polyamide (EPAm), polyvinyl pyridine, and gelatin can be mentioned.

[0025] As a non–subtlety particle, a silica particle, colloidal silica, a calcium silicate, a zeolite, a kaolinite, halloysite, a muscovite, talc, a calcium carbonate, a calcium sulfate, boehmite, pseudo-boehmite, etc. can be mentioned, for example. What has a refractive index in the range of 1.40–1.60 from the point of not reducing transparency is desirable. A silica particle is desirable in these. Moreover, the first [ an average of ] particle diameter of a non–subtlety particle has common 20nm

or less (preferably 10nm or less, especially 3–10nm), and, as for a refractive index, it is desirable that they are the 1.45 neighborhoods.

[0026] By the hydrogen bond by the surface silanol group, for an adhesion and cone reason, particles can form the structure where especially voidage is large, when especially the first [ an average of ] particle diameter is 10nm or less as mentioned above, and the ink absorption property of a silica particle improves. A silica particle is divided roughly into a wet method and dry process according to a manufacturing method. The method of the acidolysis of a silicate generating active silica, carrying out the polymerization of this moderately in a wet method, carrying out flocking settling, and obtaining a water silica is in use. One dry-process silica has a method in use of obtaining an anhydrous silica by the approach (arc process) of carrying out heating hydride generation of the approach (flame hydrolysis), silica sand, and corks by elevated-temperature gaseous-phase hydrolysis of silicon halide with an arc in an electric furnace, and oxidizing this with air. In the case of a silicic anhydride (anhydrous silica), especially voidage is easy to form the high three-dimensional structure and is desirable [ a silica ], although these water silicas and an anhydrous silica have a difference in the consistency of a surface silanol group, the existence of a hole, etc. and show a property different, respectively. This reason is 2 5–8 pieces/nm, when the consistency of a surface silanol group is a water silica, although it is not clear. Mostly, when it is easy to condense a particle densely (aggregate) and it is one anhydrous silica, it is 2 2–3 pieces/nm. Since it is few, it is presumed that it is because it becomes \*\*\*\* flocculation (FUROKYU rate) and voidage becomes high structure.

[0027] The class of resin combined with a silica particle from a viewpoint of transparency is important, and when it is an anhydrous silica, PVA, especially PVA of whenever [ low saponification ] (70 – 90% whenever [ saponification ] it is desirable) are suitable in respect of light transmission nature. Although PVA has a hydroxyl group in a structural unit, they make easy for this hydroxyl group and the silanol group of a silica particle front face to form hydrogen bond, and to form the three-dimensional network which makes the aggregated particle of a silica particle a chain unit, and it is thought that the color-material acceptance layer of the structure where voidage is high is obtained by this. Thus, not only the minute record which absorbs ink quickly by capillarity and has neither an ink blot nor ink \*\*\*\*\* is possible, but the obtained porous layer can paste up firmly the color material in thermal recording, and the toner in electrophotography record in ink jet record. This reason is because color material and a toner go underwater in the pore of a porous layer, the geometrical anchor effect which originates in a three-dimensional network as that result occurs and this fixes color material etc. firmly. Moreover, since there are many rates of a non-subtlety particle, thermal resistance is high and the embossing-proof nature in electrophotography record also has the description of being high.

[0028] The ratio (PB ratio: weight of the non-subtlety particle to the weight 1 of water soluble resin) of a non-subtlety particle (preferably silica particle) and water soluble resin has big effect also on membrane structure. If PB ratio becomes large, voidage, pore volume, and surface area (per unit weight) will become large. When a ratio exceeds 10, there is no effectiveness over film reinforcement and the cracking crack at the time of desiccation, less than by 1.5, an opening is closed by resin, voidage decreases and ink absorptivity ability falls. For this reason, the range of 1.5–10 is suitable for PB ratio. Like especially an OHP film, in order to acquire high-speed ink absorptivity with an ink jet printer, as for especially PB ratio, two or more are desirable [ to touch the image of a record sheet directly by hand, it is necessary to obtain sufficient film reinforcement, as for especially PB ratio, five or less are desirable, and ], therefore the range of 2–5 is still more suitable for PB ratio.

[0029] For example, the three-dimensional network which makes the aggregated particle of a silica particle a chain unit when the first [ an average of ] above particle diameter distributes thoroughly [ PB ratio / 2–5 ] in a water solution an anhydrous silica and water soluble resin 10nm or less and carries out spreading desiccation is formed, average pore is 30nm or less, and voidage is 50% or more and pore specific volume 0.5 ml/g. The above and specific surface area are 100m<sup>2</sup>/g. The porous membrane of the above translucency can be formed easily.

[0030] The color-material acceptance layer of this invention is a layer which hardened further the layer (porous layer) which uses the above-mentioned inorganic particle and water soluble resin as a

principal component by the cross linking agent. And in this invention, grant of a cross linking agent is performed, at the same time the above-mentioned coating liquid for porous layer formation was applied, or before the coating liquid layer for porous layer formation comes to show the falling rate of drying. The cracking crack generated by this actuation while the spreading layer of the coating liquid for porous layer formation dries can be prevented. That is, before a spreading layer comes to show the falling rate of drying at the same time the above-mentioned coating liquid for porous layer formation was applied or, the given cross linking agent content solution raises the film reinforcement of a spreading layer substantially immediately by permeating in a spreading layer, reacting promptly with the water soluble resin in a spreading layer, and making water soluble resin macromolecule-ize (hardening). Consequently, the cracking crack generated at the time of desiccation of the spreading layer of the above-mentioned coating liquid for porous layer formation can be prevented.

[0031] as the example of the cross linking agent to be used — boric acid and borate (an example, an orthoboric salt, and InBO<sub>3</sub> —) ScBO<sub>3</sub>, YBO<sub>3</sub>, LaBO<sub>3</sub>, and Mg<sub>3</sub>(BO<sub>3</sub>)<sub>2</sub>, Co<sub>3</sub>(BO<sub>3</sub>)<sub>2</sub>, diborate (an example, Mg<sub>2</sub>B—O<sub>5</sub>, Co<sub>2</sub>B—O<sub>5</sub>), a metaboric acid salt (an example, LiBO<sub>2</sub>, calcium (BO<sub>2</sub>)<sub>2</sub>, and NaBO<sub>2</sub> —) KBO<sub>2</sub> and tetraborate (example and Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> and 10H<sub>2</sub>O) 5 borate (example, KB<sub>5</sub>O<sub>8.4</sub>H<sub>2</sub>O, and calcium<sub>2</sub>B<sub>6</sub>O<sub>11</sub> and 7H<sub>2</sub>O —) CsB 5O<sub>5</sub>, glyoxal, melamine formaldehyde (an example, a methylol melamine, alkylation methylol melamine), a methylolurea, resol resin, the poly isocyanate, etc. can be mentioned. In these, boric acid or borate is desirable. Since using it combining polyvinyl alcohol as water soluble resin causes crosslinking reaction promptly, boric acid and borate have it. [desirable]

[0032] When using gelatin as water soluble resin, the following compound known as a hardening agent of gelatin can be used as a cross linking agent. Aldehyde system compounds, such as formaldehyde, glyoxal, and a glutaraldehyde; Diacetyl, Ketone system compounds, such as cyclopentane dione; screw (2-chloro ethylurea)-2-hydroxy - 4, 6-dichloro - 1, 3, 5 triazine, Activity halogenated compounds, such as 2 and 4-dichloro-6-S-triazine sodium salt; A divinyl sulfonic acid, A 1, 3-vinyl sulfonyl-2-propanol, N, and N'-ethylene screw (vinyl sulfonyl acetamido), Activity vinyl compounds, such as 1, 3, and 5-thoria chestnut roil-hexahydro-S-triazine; A dimethylolurea, N-methylol compounds, such as methylol dimethylhydantoin; Isocyanate system compound; U.S. Pat. No. 3017280, such as 1 and 6-hexamethylene di-isocyanate, Epoxy system compounds, such as carboxy imide system compound; glycerol triglycidyl ether indicated by aziridine system compound; U.S. Pat. No. 3100704 indicated by 2983611; 1, 6-hexamethylene-N, ethylene imino \*\*\*\*\*; such as an N'-bis-ethylene urea, — halogenation carboxy aldehyde system compound [, such as a mucochloric acid muco phenoxy KURORU acid, ]; — dioxane system compound; chromium alum, such as 2 and 3-dihydroxy dioxane, potash alum, a sulfuric-acid zirconium, chromium acetate, etc. Two or more sorts of these can be combined, and can also be used.

[0033] The solution of the above-mentioned cross linking agent dissolves a cross linking agent in water and/or an organic solvent, and is prepared. The concentration of a cross linking agent solution has 0.05 – 10 desirable % of the weight, and it is 0.1 – 7 % of the weight especially. Generally as a solvent of a cross linking agent, water is used. Halogenation solvents [, such as alcoholic; methyl ethyl ketone, /, such as ketone; ethyl acetate, /, such as ester; toluene, /, such as the ether such as an aromatic series solvent; tetrahydrofuran, and dichloromethane, ], such as a methanol and isopropyl alcohol, etc. can be mentioned that what is necessary is just to use what each ingredient dissolves as an organic solvent.

[0034] In this invention, when the coating liquid (coating liquid for porous layer formation) which uses a non-subtlety particle and water soluble resin as a principal component is applied on a base material, a cross linking agent is given so that this spreading layer may not cause a cracking crack, and the film reinforcement of a spreading layer is raised promptly. After applying the coating liquid which applies a cross linking agent solution to spreading and coincidence of coating liquid which use a non-subtlety particle and solubility resin as a principal component actually, or uses a non-subtlety particle and water soluble resin as a principal component, a cross linking agent solution is given promptly.

[0035] Next, after applying the coating liquid (coating liquid for porous layer formation) which uses a non-subtlety particle and water soluble resin as a principal component, before the spreading layer

comes to show the falling rate of drying, how to give a cross linking agent solution promptly is explained. the coating liquid for porous layer formation — an average of 1 [ for example, ] — the silica particle not more than order particle diameter 10nm — underwater — adding (an example —) A high-speed revolution wet colloid mill (an example, KUREA mix (M Technique Co., Ltd. make)) is used ten to 15% of the weight. For example, after carrying out distribution for 20 minutes (preferably for 10 – 30 minutes) on condition that the high-speed revolution of 10000rpm (preferably 5000 – 20000rpm), A polyvinyl alcohol water solution (it is set to PVA of about 1/3 weight of an example and a silica like) can be added, and it can obtain by distributing on the still more nearly same conditions as the above. Thus, the obtained coating liquid is a homogeneity sol and can obtain the porous layer which has a three-dimensional network by forming this on a base material by the following method of application.

[0036] Spreading of the above-mentioned coating liquid for porous layer formation can be carried out by applying the coating liquid which added the antistatic agent, the mordant, etc. to for example, the above-mentioned coating liquid further by request, and was obtained on the above-mentioned base material (film). Spreading can be performed by the well-known methods of application, such as for example, an extrusion die coating machine, the Ayr doctor coating machine, a bread coating machine, a rod coating machine, a knife coating machine, a squeeze coating machine, a reverse roll coater, and a bar coating machine.

[0037] After spreading of the coating liquid for porous layer formation, before the spreading layer comes to show the falling rate of drying, the solution containing the cross linking agent of this invention is applied on a spreading layer by the same approach as the above-mentioned coating liquid for porous layer formation, it dries and the color-material acceptance layer by which this invention was hardened is obtained. In addition, a cross linking agent solution may be given by the approach of a spray etc.

[0038] Before the above-mentioned spreading layer comes to show the falling rate of drying, the constant rate of drying which is for several minutes after immediately after spreading, and is the phenomenon in which the content of the solvent in a spreading layer decreases in proportion to time amount in the meantime is usually shown. The period which shows such the constant rate of drying is indicated by the chemical engineering handbook (707–712 pages, the Maruzen Co., Ltd. issuance, October 25, Showa 55).

[0039] After spreading of the coating liquid for porous layer formation, the color-material acceptance layer of this invention gives the above-mentioned cross linking agent content solution by the approach of spreading or a spray, while this spreading layer shows the constant rate of drying. Generally desiccation after spreading of the coating liquid for porous layer formation is performed at 50–180 degrees C for 0.5 – 10 minutes (especially for 0.5 – 5 minutes). Although this drying time naturally changes with coverage, the above-mentioned range is suitable for it.

[0040] Introductory \*\*\*\* of the cross linking agent is carried out into this spreading layer that the spreading layer is immersed in the spreading layer of the coating liquid for porous layer formation in the base material which has this spreading layer in a cross linking agent content solution within the period which shows the constant rate of drying, or by carrying out spray spreading of the cross linking agent content solution at a spreading layer. Although spreading of cross linking agent content coating liquid can use the well-known methods of application, such as a curtain flow coater besides the above-mentioned approach, an extrusion die coating machine, the Ayr doctor coating machine, a bread coating machine, a rod coating machine, a knife coating machine, a squeeze coating machine, a reverse roll coater, and a bar coating machine, its approach a coating machine does not contact a spreading layer directly using an extrusion DAI coating machine, a curtain flow coater, a bar coating machine, etc. is desirable.

[0041] The coverage on the color-material acceptance layer of cross linking agent content coating liquid is 0.01 – 10 g/m<sup>2</sup> by cross linking agent conversion. The range is common and it is 0.05–5g/m<sup>2</sup>. The range is desirable. After spreading of cross linking agent content coating liquid, generally a spreading layer is heated for 0.5 – 30 minutes at 40–180 degrees C, and desiccation and hardening are performed. It is desirable to heat in 1 – 20 minutes at 40–150 degrees C. For example, when using boric acid as a cross linking agent, it is desirable to heat for 5 – 20 minutes at 60–100 degrees C.

[0042] Next, how to apply a cross linking agent solution to spreading and coincidence of the coating liquid (coating liquid for porous layer formation) which uses as a principal component the non-subtlety particle and water soluble resin which are the another formation approach of the color-material acceptance layer of this invention is explained. It can obtain by carrying out simultaneous spreading and stiffening the coating liquid for porous layer formation, and a cross linking agent content solution on a base material, so that the coating liquid for porous layer formation may contact a base material. Simultaneous spreading of the coating liquid for porous layer formation and a cross linking agent content solution can be performed by the method of application which uses for example, an extrusion DAI coating machine and a curtain flow coater, for example. Generally desiccation after simultaneous spreading (multistory spreading) is performed by heating for 0.5 – 10 minutes at 40–150 degrees C, and a spreading layer is hardened. It is desirable to heat for 0.5 – 5 minutes at further 40–100 degrees C. For example, when using boric acid as a cross linking agent, it is desirable to heat for 5 – 20 minutes at 60–100 degrees C.

[0043] When the above-mentioned multistory spreading is performed for example, by the extrusion die coating machine, multistory is formed before two sorts of coating liquid moves on an extrusion die coating machine, i.e., a base material. And since crosslinking reaction has already occurred by the interface of a bilayer in case the spreading layer (multistory) of a bilayer moves to a base material, it becomes easy to generate thickening by mixing of regurgitation coating liquid near the delivery of an extrusion die coating machine, and trouble may be caused to spreading actuation. Therefore, in case the above-mentioned simultaneous spreading is performed, it is desirable to apply further, a cross linking agent and the liquid which does not react three layers of coincidence with spreading of the coating liquid for porous layer formation and this cross linking agent content solution, so that a layer may be intervened between the layer of coating liquid and the layer of a solution. As a cross linking agent and liquid which does not react, a minute amount \*\*\*\* water solution can be mentioned for a cross linking agent and the water soluble resin (it is used as a thickener) which does not react, for example.

[0044] Moreover, the obtained color-material acceptance layer can raise surface smooth nature, transparency, and paint film reinforcement after spreading and desiccation by letting between roll nips pass under heating and application of pressure using a super calender, gloss calender, etc. However, decline in voidage needs to perform such processing by setting up few conditions in order to reduce voidage (namely, in order for ink absorptivity to fall).

[0045] In the case of ink jet record, the thickness of the obtained color-material acceptance layer needs to have the absorption capacity which absorbs all drops, and it is necessary to determine this in connection with the voidage of a paint film. For example, the amount of ink is 2 8 nL(s)/mm. If it is the case where voidage is 60%, film about 15 micrometers or more is needed for thickness. In ink jet record, the thickness of the range of 10–50 micrometers is desirable. In the case of thermal ink transfer printing or an electrophotography method, since color material or a toner is adsorbed on a front face, a thin film is enough, and it is desirable. [ of 0.1–10-micrometer thickness ]

[0046] Moreover, a single raw material is sufficient as the non-subtlety particle and water soluble resin which mainly constitute the above-mentioned color-material acceptance layer, respectively, and the mixed stock of two or more raw materials is sufficient as them. moreover, the color-material acceptance layer may contain acid alkali as various kinds of mineral and a PH regulator, in order are alike other than this and to raise the dispersibility of a particle, although it mainly consists of the above-mentioned inorganic particle and water soluble resin. Moreover, various kinds of surfactants for the object which raises spreading fitness and surface quality may be used. In order to control surface frictional electrification and exfoliation electrification, or in order to adjust surface electric resistance in a xerography, the metallic-oxide particle with a surfactant with ion conductivity or electronic conductivity may be included. Moreover, a mordant may be used in order to fix coloring matter in ink jet record and to raise a water resisting property. Moreover, various kinds of mat agents for the object which reduces a surface friction property may be included. Furthermore, various kinds of antioxidants for the object which controls degradation of color material again, and an ultraviolet ray absorbent may be included.

[0047] Moreover, between a color-material acceptance layer and a base material, an adhesive property may be raised or undercoat may be prepared for the object of adjusting electric

resistance. Furthermore, a color-material acceptance layer may be prepared in both sides, in order to prepare in one side of a base material and to control curl etc. Moreover, an antireflection film may be prepared, in order to raise light transmission nature to the reverse side or both sides when preparing a color-material acceptance layer only in one side in using by OHP etc.

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[Translation done.]

## \* NOTICES \*

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- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\*\* shows the word which can not be translated.
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## EXAMPLE

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[Example]

[0049] [Example 1]

(1) The presentation of the coating liquid for porous layer (front [ bridge formation ] color-material acceptance layer) formation (all the values of the weight section which shows the loadings of all the following coating liquid express solid content or a nonvolatile matter)

\*\* Anhydrous silica particle (primary [ an average of ] particle diameter : 7nm; 10 weight section surface silanol group : 2–3 pieces/nm<sup>2</sup>; refractive index : 1.45;)

Aerosil 300 (product made from Japanese Aerosil)

\*\* Polyvinyl alcohol (it is the 81.8%; 3.3 weight section whenever [ saponification ] polymerization-degree 4000–VA440 (Kuraray Co., Ltd. make))

\*\* ion exchange water the polyvinyl alcohol water solution (what was dissolved in the remainder 62.7 weight section of ion exchange water) after adding in the ion exchange water (73.3 weight sections) of \*\* and distributing the silica particle of 136.0 weight sections \*\* for 20 minutes on condition that 10000rpm using a high-speed revolution wet colloid mill (KUREA mix (M Technique Co., Ltd. make)) — in addition, it distributed on the still more nearly same conditions as the above, and the coating liquid for porous layer formation was obtained.

[0050] An extrusion die coating machine is used for the front face of the laminated paper for the photographic printing papers with a thickness of 200 micrometers for the above-mentioned coating liquid, and it is 200 cc/m<sup>2</sup>. It applied by coverage and dried for 3 minutes at 80 degrees C (3m [/second] wind speed) with hot air drying equipment. The spreading layer showed the constant rate of drying in the meantime. For these 3 minutes, after desiccation, promptly, this spreading layer was made immersed in the boric acid content solution of following (2) for 1 second, and it dried for 10 minutes at 80 degrees C. Thereby, desiccation thickness formed the color-material acceptance layer which is 27 micrometers.

[0051]

(2) Boric acid content solution \*\* boric acid 1 Weight section \*\* surfactant (F-144D, Dainippon Ink & Chemicals, Inc. make) 0.2 weight section \*\* ion exchange water The 98.8 weight sections [0052]

(3) Presentation \*\*M-100C of a silane coupling agent solution which has quarternary ammonium salt (Sumitomo Chemical Co., Ltd. make) 1.6 weight section \*\* Para toluenesulfonic acid (10-% of the weight methanol solution) 1.6 weight sections \*\* silane coupling agent (AZ-6160, Nippon Unicar make) 4.0 weight sections \*\* methanol #3.1 bar coating machine is used for the 32.8 weight sections above-mentioned silane coupling agent solution on the above-mentioned color-material acceptance layer, and it is 2.1g/m<sup>2</sup>. It applies by coverage (solid content) and heats for 5 minutes at 80 degrees C after that. The color-material acceptance layer processed by the silane coupling agent which has quarternary ammonium salt was formed. The sheet for record for ink jets was obtained as mentioned above.

[0053] Except having used the following coating liquid for the coating liquid for [example 2] porous layer (front [ bridge formation ] color-material acceptance layer) formation, like the example 1, formation of a color-material acceptance layer and processing of a silane coupling agent were performed, and the sheet for record for ink jets was obtained.

(1) The presentation of the coating liquid for porous layer (front [ bridge formation ] color-material

acceptance layer) formation (all the values of the weight section which shows the loadings of all the following coating liquid express solid content or a nonvolatile matter)

\*\* Dry type silica particle (primary [ an average of ] particle diameter : 7nm; 10 weight section surface silanol group : 2-3 pieces/nm 2; refractive index : 1.45;)

Aerosil 300 (product made from Japanese Aerosil)

\*\* Polyvinyl alcohol (it is the 81.8%; 3.0 weight section whenever [ saponification ] polymerization-degree 4000-VA440 (Kuraray Co., Ltd. make))

\*\* Vinyl pyrrolidone/dimethylaminoethyl The 1.5 weight sections The 4th class salt copolymer of methacrylate (the ruby cut PQ11, BASF Japan, Ltd. make) \*\* ion exchange water The 136.0 weight sections [0054] \*\* Add a silica particle in the ion exchange water (73.3 weight sections) of \*\*, the polyvinyl alcohol water solution (what was dissolved in the remainder 62.7 weight section of ion exchange water) after making it distribute for 20 minutes on condition that 10000rpm using a high-speed revolution wet colloid mill (KUREA mix (M Technique Co., Ltd. make)), and the copolymer of \*\* — in addition, it distributed on the still more nearly same conditions as the above, subsequently to 8-9 pH was adjusted, and the coating liquid for porous layer formation was obtained.

[0055] In the [example 1 of comparison] example 1, the sheet for record for ink jets was similarly produced except having not applied the boric acid content solution of (2).

[0056] In the [example 2 of comparison] example 2, the sheet for record for ink jets was similarly produced except having not applied the boric acid content solution of (2).

[0057] In the [example 3 of comparison] example 1, the sheet for record for ink jets was similarly produced except having changed the desiccation for 3 minutes into desiccation for 4 minutes at this temperature by 80 degrees C (3m [/second] wind speed) with hot air drying equipment (the spreading layer having shown the falling rate of drying in the meantime).

[0058] About the sheet for record for ink jets obtained above, the ink jet fitness was evaluated by the following measuring methods.

(1) Parallel ray permeability was measured using the Hayes hazemeter (HGM-2DP; Suga Test Instruments Co., Ltd. make), and Hayes was obtained. However, in each example and the example of a comparison, above-mentioned Hayes was measured using the sheet for record which used the polyethylene terephthalate film with a thickness of 100 micrometers instead of the laminated paper for the photographic printing papers as a base material, and was obtained.

[0059] (2) It measured using the voidage mercury porosimeter (pore sizer 9320-PC2, Shimadzu Make), distribution was acquired, and the average was calculated.

(3) About the record sheet obtained the degree of gloss, glossiness was measured according to the approach of a publication to JIS-P -8142 (75-degree specular gloss test method of paper and the paper board).

[0060] (4) With the ink rate-of-absorption ink jet printer (PM-700C; Seiko Epson make), Y (yellow), M (Magenta), C (cyanogen), K (black), B (blue), G (green), and R (red) to the sheet for record carried out solid printing, the contact press of the paper was carried out just behind that (after about 10 seconds), and it judged as follows by the existence of the imprint to the paper of ink.  
AA: Ink was not imprinted by paper.

CC: Ink was imprinted by paper.

(5) the sheet for generating profit \*\*\*\* record of a cracking crack was observed visually, and it evaluated as follows according to the existence of the cracking crack generated on the front face, and its magnitude.

AA: The result of the above-mentioned assessment as which the cracking crack of the die length beyond CC:3mm as which the cracking crack of the die length which is BB:1-2mm as which a cracking crack is not regarded is regarded is shown in the following table 1.

[0061]

[A table 1]

Table 1 . \*\*\*\*\* \*|[|] \*\* - \*\* \*\*\*\*\* . \*\*\*\* \* .

\*\*\*\*\* The \*\*\*\* method The \*\*\*\* method The \*\*\*\* method \*\*\*\*\* \*|\* ..  
\*\*\*\*\* . \*\*\* I forerunner . \*\*\* . \*\*\* . \*\*\* . \*\*\*\*\* . \*\*\* | \*\* . \*\*\* . \*\*\*\*\* .  
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[Translation done.]

(19)日本国特許庁 (JP)

(12) 公開特許公報 (A)

(11)特許出願公開番号

特開平11-115308

(43)公開日 平成11年(1999)4月27日

(51)Int.Cl.<sup>6</sup>

B 41 M 5/00  
B 41 J 2/01

識別記号

F I

B 41 M 5/00  
B 41 J 3/04

B

101Y

審査請求 未請求 請求項の数9 FD (全 9 頁)

(21)出願番号 特願平9-296285

(22)出願日 平成9年(1997)10月14日

(71)出願人 000005201

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(54)【発明の名称】 記録用シート

(57)【要約】

【課題】 インクジェット記録、熱転写記録又は電子写真記録により画像シートを得ることができ、そして、塗布乾燥時にヒビ割れが発生することなく簡易に形成することができる色材受容層を有する記録用シートを提供すること。

【解決手段】 支持体上に色材受容層が設けられた記録用シートであって、その色材受容層が、無機微粒子と水溶性樹脂とを含む塗布液を支持体上に塗布し、その塗布と同時に、あるいは塗布した層が恒率乾燥速度を示す間(減率乾燥速度を示すようになる前)に、その水溶性樹脂を架橋させることができる架橋剤を含む溶液を塗布等の方法で付与して、硬化させることにより得られた層であることを特徴とする記録用シート。

## 【特許請求の範囲】

【請求項1】 支持体上に色材受容層が設けられてなる記録用シートにおいて、該色材受容層が、無機微粒子及び水溶性樹脂を含む塗布液を支持体上に塗布し、該塗布とともに、あるいは該塗布した層が減率乾燥速度を示すようになる前に、該水溶性樹脂を架橋させることができる架橋剤を含む溶液を付与し、硬化させることにより得られた層であることを特徴とする記録用シート。

【請求項2】 架橋剤が硼酸または硼酸塩である請求項1に記載の記録用シート。

【請求項3】 無機微粒子が、平均1次粒子径が20nm以下のシリカ微粒子である請求項1又は2に記載の記録用シート。

【請求項4】 水溶性樹脂がポリビニルアルコールである請求項1～3のいずれかに記載の記録用シート。

【請求項5】 無機微粒子と水溶性樹脂の重量比が1.5：1～10：1の範囲にある請求項1～4のいずれかに記載の記録用シート。

【請求項6】 上記色材受容層が40～80%の空隙率を有する請求項1～5のいずれかに記載の記録用シート。

【請求項7】 上記色材受容層が、塩基性基を有するシランカップリング剤を含む請求項1～6のいずれかに記載の記録用シート。

【請求項8】 該色材受容層が、無機微粒子及び水溶性樹脂を含む塗布液と該架橋剤の溶液とを同時塗布する際に、さらに該架橋剤と反応しない液を、塗布液の層と架橋剤の溶液の層との間にその液の層が介在するように同時塗布し、硬化させることにより得られた層である請求項1～7のいずれかに記載の記録用シート。

【請求項9】 インクジェット記録用である請求項1～8のいずれかに記載の記録用シート。

## 【発明の詳細な説明】

## 【0001】

【産業上の利用分野】本発明は、色材を用いて記録する記録シートに関するものである。特に、インクジェット記録、熱転写記録及び電子写真記録等により画像シートを形成するために有利に用いられる記録シートに関する。

## 【0002】

【従来の技術】近年、情報産業の急速な発展に伴い、種々の情報処理システムが開発され、また、それぞれの情報システムに適した記録方法及び装置も開発され、採用されている。このような記録方法の中で、インクジェットあるいはプロッタを用いたインク記録、および溶融型色材あるいは昇華型色材を用いた感熱転写記録においては、使用する装置が軽量化とコンパクト化され、騒音もなく、操作性、保守性にも優れたものとなっている。さらに、このような記録方法で使用される装置はカラー化も容易であることから、最近広く使用されている。ま

た、従来の電子写真方式においてもカラー化が進み、高解像度でフルカラーのプリンタや複写機が開発され、商品化されてきている。

【0003】インクジェット方式は各種の方式が開発されているが、物性的には大きく分けて水溶性色素を含む色素溶液（水性インク）を用いる方法、及び油溶性色素を含む色素溶液（油性インク）を用いる方法、そして色素を含有する低融点固体ワックス（ワックスインク）を熱溶融させて用いる方法の三種がある。主流は水性インクを使用するタイプである。何れにしてもインク記録シートの表面に液状の微粒滴を吐出させて画像を形成する方法である。

【0004】感熱転写方式は、大きく分けて二種の方式がある。第1の方式は、支持体上に塗工された熱溶融性のインクを支持体側からの熱印加により、熱印加したパターン状に溶融させることによって、記録シートに転写させて画像を得る方法（溶融熱転写）であり、第2の方式は、支持体上に高軟化点の樹脂と昇華性染料とからなる感熱記録材料に、前者と同様に支持体側からの熱印加を行ない、熱印加したパターン状に昇華染料を昇華させることにより記録シートに転写させて画像を得る方法（昇華熱転写）である。電子写真方式は、帯電した光導電層に光画像パターンを与えて静電潜像を形成し、次いでトナー現像後に記録シートに転写し、熱でトナーを溶融定着する方法が主流である。

【0005】一方、次のような用途では、透明シートを使用する必要があり、多くは表面に色材受容（吸収）層を設けた透明フィルムを用いて、上記のように画像形成して記録シートを作成する。例えば、会議等でスライドの代わりに使用される機会が増えているOHPフィルム、印刷ポスターや表示板の代わりに使用される機会が増えているバックライトディスプレイ用フィルム、及び第二原図用フィルム等を挙げることができる。

【0006】上記の記録方式で画像が形成された透明フィルムは、得られる画像の色相、彩度、明度に加えて、色材が記録シートの表面に強固に接着していることが必要であり、さらにインクジェット記録の場合では、精細な画像を得る上で、液状インクを早く吸収し、インク滲みやインク溜まりの無いこと等が要求される。

【0007】これらの問題点を解決するために、従来から様々な提案がなされている。例えば、特開昭57-14091号公報および特開昭61-19389号公報には、透明支持体と、その上に設けられたコロイダルシリカと水溶性樹脂との透明層からなる記録用シートが提案されている。しかしながら、この透明層は、コロイダルシリカの粒子が大きすぎ、また水溶性樹脂の量が多過ぎるため充分に大きな空隙率が得られず、このため上記記録用シートは充分に大きいインキ吸収速度を示しにくいという問題がある。

【0008】また、特開平2-276670号公報およ

び特開昭3-281383号公報には、擬ベーマイト微粒子から形成された細孔を有する色材受容層を具備した記録用シートが開示されている。本発明者の検討によれば、この記録用シートはインキ吸収性は向上するものの、屈折率が1.65と高いため、充分に高い透明度が得られないことが判明した。

【0009】さらにまた、特開昭61-53598号公報には、支持体と、その上に設けられた合成シリカ、屈折率1.44～1.55の微粒子及び水溶性樹脂からなる透明層を有する記録用シートが開示されている。合成シリカは、通常10nmを超える一次粒子径を有し、更に二次粒子は数100nmの粒径となる。このような二次粒子は、光を散乱し易く、従ってこのような粒子を含む記録用シートは、充分に高い光線透過率を示さない。更に、透明層が大きな二次粒子のため比、較的多きな空孔を有するので、インキ滲みやインク溜まりの発生を充分に防止することができない。

【0010】上記問題を解決した記録用シートとして、特開平7-276789号公報に、無機微粒子と水溶性樹脂とから形成された高い空隙率の三次元構造を有する色材受容層が透明支持体上に設けられた記録用シートが提案されている。この構成により、上記インキ吸収性と混色滲みの抑制が充分で、解像度が高い画像を得ることができるとされている。

#### 【0011】

【発明が解決しようとする課題】無機微粒子及び水溶性樹脂から形成された高い空隙率の色材受容層は、一般に粒子が小さく、また粒子の含有量も大きい。そして、このような色材受容層を形成するための材料を含有する塗布液を塗布した際、塗布層を乾燥させている間にヒビ割れが発生する場合があることが本発明者の検討により明らかとなつた。そして、このヒビ割れは特に、乾燥時間を短縮するために、比較的高い温度で乾燥した場合に発生し易いことが明らかとなつた。このヒビ割れを防止する方法として、特開平9-109545号公報に、塗布液のバインダーの粘度を比較的高くする方法が提案されているが、この方法では、塗布ムラ等が発生し易く、作業性の低下につながるので好ましくない。また、この方法は、ヒビ割れ防止効果においても十分とは言えない。

【0012】上記色材受容層のヒビ割れを防止するため、本発明者が検討を重ねたところ、塗布層のヒビ割れは、支持体上に色材受容層形成用塗布液を塗布した後、その乾燥途中、即ち恒率乾燥から減率乾燥へ移行する時期に発生することが明らかとなつた。この知見を基に、本発明者は更に検討を重ね、減率乾燥状態が始まる前の恒率乾燥の状態において、できるだけ早く塗布層の膜強度を高めることにより、ヒビ割れを防止が可能であることを見いだし、本発明に到達した。

【0013】従って、本発明はインクジェット記録、熱転写記録又は電子写真記録により画像シートを得ること

ができ、そして、塗布乾燥時にヒビ割れが発生しにくく、簡易に形成することができる色材受容層を有する記録用シートを提供することを目的とする。

【0014】特に、本発明は、液状インクを迅速に吸収してインクの吸収ムラがなく、インク滲みやインク溜まりの無い精細な画像を得ることができ、そして、塗布乾燥時にヒビ割れが発生することなく、簡易に形成することができる色材受容層を有するインクジェット記録に適した記録用シートを提供することを目的とする。

#### 【0015】

【課題を解決するための手段】本発明は、支持体上に色材受容層が設けられてなる記録用シートにおいて、該色材受容層が、無機微粒子及び水溶性樹脂を含む塗布液を支持体上に塗布し、該塗布と同時に、あるいは該塗布した層が減率乾燥速度を示すようになる前に、該水溶性樹脂を架橋させることができる架橋剤を含む溶液を付与し、硬化させることにより得られた層であることを特徴とする記録用シートにある。

【0016】上記本発明の記録用シートの好ましい態様は下記のとおりである。

- (1) 架橋剤が硼酸又は硼酸塩である。
- (2) 無機微粒子が、平均1次粒子径が20nm以下(好ましくは、10nm以下、特に3～10nmの範囲)のシリカ微粒子である。

(3) 水溶性樹脂がポリビニルアルコールもしくはゼラチンである。

(4) 無機微粒子と水溶性樹脂の重量比が1.5：1～10：1の範囲にある。

(5) 色材受容層が40～80%の空隙率(特に50～80%の空隙率)を有する。

【0017】(6) 色材受容層が、塩基性基(特に第四級アンモニウム塩基)を有するシランカップリング剤を含む

(7) 色材受容層が、無機微粒子及び水溶性樹脂を含む塗布液と該架橋剤の溶液とを同時塗布する際に、さらに該架橋剤と反応しない液を、塗布液の層と架橋剤の溶液の層との間にその液の層が介在するように同時塗布し、硬化させることにより得られた層である。

(8) 記録用シートがインクジェット記録用である。

【0018】(9) 架橋剤含有溶液の色材受容層上の塗布量が、架橋剤換算で0.01～10g/m<sup>2</sup>の範囲(0.05～5g/m<sup>2</sup>の範囲)にある。

(10) 色材受容層が三次元網目構造を有する。

(11) 色材受容層が30%以下のヘイズを有する。

(12) 色材受容層の層厚が10～50μmであるインクジェット記録用の上記記録用シート。

(13) 色材受容層の層厚が0.1～10μmである電子写真用又は感熱記録用上記記録用シート。

#### 【0019】

【発明の実施の形態】本発明の記録用シートは、支持体

と、支持体上に形成された色材受容層とからなる基本構成を有し、例えば下記のようにして製造することができる。

【0020】上記支持体として使用できる材料としては、プラスチック等の透明材料を用いても、紙等の不透明な材料を用いても良い。本発明では、色材受容層の透明性を生かす上で、支持体は透明支持体または高光沢の不透明支持体であることが好ましい。透明支持体として使用できる材料としては、透明でOHPあるいはバックライトディスプレイで使用される時の輻射熱に耐える性質を有する材料が好ましい。このような材料としては、ポリエチレンテレフタレート等のポリエステル類；ニトロセルロース、セルロースアセテート、セルロースアセテートブチレート等のセルロースエステル類、そしてポリスルホン、ポリフェニレンオキサイド、ポリイミド、ポリカーボネート、ポリアミド等を挙げることができる。これらの中でポリエステル類が好ましく、特にポリエチレンフタレートが好ましい。透明支持体の厚さは、特に制限はないが、50～200μmのものが取り扱い易く好ましい。

【0021】高光沢の不透明支持体としては、色材受容層の設けられる側の表面が40%以上の光沢度を有するものが好ましい。上記光沢度は、JIS P-8142(紙及び板紙の75度鏡面光沢度試験方法)に記載の方法に従って測定することにより求められる値である。高光沢の不透明支持体の例としては、アート紙、コート紙、キャストコート紙、銀塩写真用支持体等に使用されるバライタ紙等の高光沢の紙；ポリエチレンテレフタレート(PET)等のポリエステル類、ニトロセルロース、セルロースアセテート及びセルロースアセテートブチレート等のセルロースエステル類、あるいはポリスルホン、ポリフェニレンオキサイド、ポリイミド、ポリカーボネート、ポリアミド等のプラスチックフィルムで、このフィルムに白色顔料等を含有させて不透明にした高光沢の(表面カレンダー処理等を行なって)フィルム、あるいは上記各種紙、上記透明プラスチックフィルムまたは白色顔料等含有プラスチックの表面に、白色顔料を含有するか、あるいは含有しないポリオレフィンの被覆層が設けられたフィルム等を挙げることができる。さらに、白色顔料含有発泡ポリエステルフィルム(例、ポリオレフィン微粒子を含有させ、延伸により空隙を形成したカルシウム含有発泡PET)も挙げができる。また銀塩写真用支持体として一般的に使用されているポリオレフィンコート紙(表面に白色顔料含有ポリオレフィン層が設けられた紙支持体等のポリオレフィンの被覆層が設けられた支持体の一種)、あるいは金属蒸着層等が設けられた特種紙等を、好適に使用することができる。特に白色顔料含有ポリオレフィン層が設けられた紙支持体、白色顔料含有ポリオレフィン層が設けられたポリエステル(好ましくはPET)フィルム、白色顔料含

有ポリエステルフィルムあるいは白色顔料含有発泡ポリエステルフィルムが好ましい。不透明支持体の厚さは、特に制限はないが、50～200μmのものが取り扱い易く好ましい。

【0022】また支持体はコロナ放電処理、火炎処理、紫外線照射処理を施したものを使用してもよい。

【0023】本発明の色材受容層は、無機微粒子と水溶性樹脂とを含む塗布液を支持体上に塗布する際、該塗布と同時に、あるいは該塗布した層が減率乾燥速度を示すようになる前に塗布層上に、架橋剤の溶液を付与し、硬化させることにより得られる水溶性樹脂が架橋剤により硬化した層である。

【0024】水溶性樹脂の例としては、親水性構造単位としてヒドロキシル基を有する樹脂である、ポリビニルアルコール(PVA)、セルロース系樹脂(メチルセルロース(MC)、エチルセルロース(EC)、ヒドロキシエチルセルロース(HEC)、カルボキシメチルセルロース(CMC)等)、キチン類、及びデンプン；エーテル結合を有する樹脂であるポリエチレンオキサイド(PEO)、ポリプロピレンオキサイド(PPG)、ポリエチレングリコール(PEG)及びポリビニルエーテル(PVE)；そしてアミド基またはアミド結合を有する樹脂であるポリアクリラミド(PAAM)およびポリビニルピロリドン(PVP)を挙げることができる。また、解離性基としてカルボキシル基を有するポリアクリル酸塩、マレイン酸樹脂、アルギン酸塩及びゼラチン類；スルホン基を有するポリスチレンスルホン酸塩、アミノ基、イミノ基、第3アミン及び第4級アンモニウム塩を有するポリアリルアミン(PAA)、ポリエチレンイミン(PEI)、エポキシ化ポリアミド(EPA)、ポリビニルピリジン及びゼラチン類を挙げることができる。

【0025】無機微粒子としては、例えば、シリカ微粒子、コロイダルシリカ、珪酸カルシウム、ゼオライト、カオリナイト、ハロイサイト、白雲母、タルク、炭酸カルシウム、硫酸カルシウム、ベーマイト、擬ベーマイト等を挙げることができる。透明性を低下させない点から、屈折率が1.40～1.60の範囲にあるものが好ましい。これらの中でシリカ微粒子が好ましい。また無機微粒子の平均一次粒子径は20nm以下(好ましくは10nm以下、特に3～10nm)が一般的で、また屈折率は1.45附近であることが好ましい。

【0026】シリカ粒子は、表面のシラノール基による水素結合により粒子同士が付着やすい為、上記のように平均一次粒子径が特に10nm以下の場合に特に空隙率の大きい構造を形成することができ、インク吸収特性が向上する。シリカ粒子は製造法により湿式法と乾式法に大別される。湿式法では、ケイ酸塩の酸分解により活性シリカを生成し、これを適度に重合させ凝集沈降させ含水シリカを得る方法が主流である。一方の乾式法シリカ

は、ハロゲン化珪素の高温気相加水分解による方法（火炎加水分解法）、ケイ砂とコークスを電気炉中でアークにより加熱還元化し、これを空気で酸化する方法（アーク法）で無水シリカを得る方法が主流である。これらの含水シリカ及び無水シリカは、表面のシラノール基の密度、空孔の有無等に相違があり、それぞれ異なった性質を示すが、無水珪酸（無水シリカ）の場合に特に空隙率が高い三次元構造を形成し易く好ましい。この理由は明らかではないが、表面のシラノール基の密度が含水シリカの場合には5～8個/ $\text{nm}^2$ と多く粒子が密に凝集（アグリゲート）し易く、一方の無水シリカの場合は2～3個/ $\text{nm}^2$ と少ない為、粗な軟凝聚（フロキュレート）となり空隙率が高い構造になるためであると推定される。

【0027】透明性の観点から、シリカ微粒子に組み合わせる樹脂の種類が重要であり、無水シリカの場合は、PVA、特に低鹹化度（好ましくは鹹化度70～90%）のPVAが光透過性の点で好適である。PVAは、構造単位に水酸基を有するが、この水酸基とシリカ粒子表面のシラノール基が水素結合を形成して、シリカ粒子の二次粒子を鎖単位とする三次元網目構造を形成し易くし、これにより、空隙率の高い構造の色材受容層が得られると考えられる。このようにして得た多孔質層はインクジェット記録において、毛細管現象によって急速にインクを吸収し且つインクにじみやインク溜まりの無い精細な記録が可能であるばかりでなく、感熱記録における色材、そして電子写真記録におけるトナーを強固に接着できる。この理由は、色材やトナーが多孔質層の細孔内にもぐり込み、その結果として三次元網目構造に起因する形状的なアンカー効果が発生し、それにより色材等を強固に固定する為である。また、無機微粒子の割合が多い為、耐熱性が高く電子写真記録に於ける耐エンボス性も高いという特徴がある。

【0028】無機微粒子（好ましくはシリカ微粒子）と水溶性樹脂の比率（PB比：水溶性樹脂の重量1に対する無機微粒子の重量）は、膜構造にも大きな影響を与える。PB比が大きくなると空隙率、細孔容積、表面積（単位重量当たり）が大きくなる。比率が10を超えた場合には、膜強度、乾燥時のヒビ割れに対する効果がなく、1.5未満では空隙が樹脂で塞がれ、空隙率が減少してインク吸収性能が低下する。この為、PB比は1.5～10の範囲が好適である。特にOHPフィルムのように、記録シートの画像に手で直接触る場合は充分な膜強度を得る必要があり、PB比は5以下が特に好ましく、またインクジェットプリンタで高速インク吸収性を得る為にはPB比は2以上が特に好ましく、従ってPB比は2～5の範囲がさらに好適である。

【0029】例えば、上述のような平均一次粒子径が10nm以下の無水シリカと水溶性樹脂をPB比が2～5で水溶液中に完全に分散し塗布乾燥した場合、シリカ粒

子の二次粒子を鎖単位とする三次元網目構造が形成され、平均細孔が30nm以下、空隙率が50%以上、細孔比容積0.5ml/g以上、そして比表面積が100m<sup>2</sup>/g以上の透光性の多孔質膜を容易に形成することができる。

【0030】本発明の色材受容層は、上記無機微粒子及び水溶性樹脂を主成分とする層（多孔質層）を、さらに架橋剤により硬化した層である。しかも、本発明では、架橋剤の付与は、上記多孔質層形成用塗布液が塗布されたと同時に、あるいは多孔質層形成用塗布液層が減率乾燥速度を示すようになる前に行なわれる。この操作により、多孔質層形成用塗布液の塗布層が乾燥する間に発生するヒビ割れを防止することができる。即ち、上記多孔質層形成用塗布液が塗布されたと同時に、あるいは塗布層が減率乾燥速度を示すようになる前に、付与された架橋剤含有溶液は塗布層内に浸透し、塗布層内の水溶性樹脂と速やかに反応し、水溶性樹脂を高分子化（硬化）させることにより、塗布層の膜強度を即時に大幅に向上させる。その結果、上記多孔質層形成用塗布液の塗布層の乾燥時に発生するヒビ割れを防止することができる。

【0031】用いる架橋剤の例としては、硼酸、硼酸塩（例、オルト硼酸塩、InBO<sub>3</sub>、ScBO<sub>3</sub>、YBO<sub>3</sub>、LaBO<sub>3</sub>、Mg<sub>3</sub>(BO<sub>3</sub>)<sub>2</sub>、Co<sub>3</sub>(BO<sub>3</sub>)<sub>2</sub>、二硼酸塩（例、Mg<sub>2</sub>B<sub>2</sub>O<sub>5</sub>、Co<sub>2</sub>B<sub>2</sub>O<sub>5</sub>）、メタ硼酸塩（例、LiBO<sub>2</sub>、Ca(BO<sub>2</sub>)<sub>2</sub>、NaBO<sub>2</sub>、KBO<sub>2</sub>）、四硼酸塩（例、Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>・10H<sub>2</sub>O）、五硼酸塩（例、KB<sub>5</sub>O<sub>8</sub>・4H<sub>2</sub>O、Ca<sub>2</sub>B<sub>6</sub>O<sub>11</sub>・7H<sub>2</sub>O、CsB<sub>5</sub>O<sub>8</sub>）、グリオキザール、メラミン・ホルムアルデヒド（例、メチロールメラミン、アルキル化メチロールメラミン）、メチロール尿素、レンール樹脂、ポリイソシアネート等を挙げることができる。これらの中で、硼酸あるいは硼酸塩が好ましい。硼酸、硼酸塩は、水溶性樹脂としてポリビニルアルコールと組み合わせて使用することが、速やかに架橋反応を起こすので好ましい。

【0032】水溶性樹脂としてゼラチンを用いる場合には、ゼラチンの硬膜剤として知られている、下記の化合物を架橋剤として用いることができる。ホルムアルデヒド、グリオキザール、グルタルアルデヒド等のアルデヒド系化合物；ジアセチル、シクロペンタンジオン等のケトン系化合物；ビス（2-クロロエチル尿素）-2-ヒドロキシ-4、6-ジクロロ-1、3、5トリアジン、2、4-ジクロロ-6-S-トリアジン・ナトリウム塩等の活性ハロゲン化合物；ジビニルスルホン酸、1、3-ビニルスルホニル-2-プロパノール、N、N'-エチレンビス（ビニルスルホニアセタミド）、1、3、5-トリアクリロイル-ヘキサヒドロ-S-トリアジン等の活性ビニル化合物；ジメチロール尿素、メチロールジメチルヒダントイン等のN-メチロール化合物；1、6-ヘキサメチレンジイソシアネート等のイソ

シアネート系化合物；米国特許明細書第3017280号、同第2983611号に記載されたアジリジン系化合物；米国特許明細書第3100704号に記載されるカルボキシミド系化合物；グリセロールトリグリシルエーテル等のエポキシ系化合物；1、6-ヘキサメチレン-N、N'-ビスエチレン尿素等のエチレンイミノ系化合物；ムクロロ酸ムコフェノキシクロロ酸等のハロゲン化カルボキシアルデヒド系化合物；2、3-ジヒドロキシジオキサン等のジオキサン系化合物；クロム明ばん、カリ明ばん、硫酸ジルコニウム、酢酸クロム等。これらは二種以上組み合わせて用いることができる。

【0033】上記架橋剤の溶液は、架橋剤を水及び／又は有機溶剤に溶解して調製される。架橋剤溶液の濃度は、0.05～1.0重量%が好ましく、特に0.1～7重量%である。架橋剤の溶媒としては、一般に水が使用される。有機溶剤としては、各材料が溶解するものを使用すれば良く、例えば、メタノール、イソプロピルアルコール等のアルコール；メチルエチルケトン等のケトン；酢酸エチル等のエステル；トルエン等の芳香族溶剤；テトラヒドロフラン等のエーテル及びジクロロメタン等のハロゲン化溶剤等を挙げることができる。

【0034】本発明では、無機微粒子及び水溶性樹脂を主成分とする塗布液（多孔質層形成用塗布液）を支持体上に塗布した際、該塗布層がヒビ割れを起こさないように架橋剤を付与し、速やかに塗布層の膜強度を向上させている。実際には、無機微粒子と溶性樹脂とを主成分とする塗布液の塗布と同時に架橋剤溶液を塗布するか、無機微粒子と水溶性樹脂とを主成分とする塗布液を塗布した後、速やかに架橋剤溶液が付与される。

【0035】次に、無機微粒子と水溶性樹脂とを主成分とする塗布液（多孔質層形成用塗布液）を塗布した後、その塗布層が減率乾燥速度を示すようになる前に速やかに架橋剤溶液を付与する方法について説明する。多孔質層形成用塗布液は、例えば、平均一次粒子径10nm以下のシリカ微粒子を水中に添加して（例、1.0～1.5重量%）、高速回転湿式コロイドミル（例、クレアミックス（エム・テクニック（株）製））を用いて、例えば10000rpm（好ましくは5000～20000rpm）の高速回転の条件で20分間（好ましくは1.0～3.0分間）分散させた後、ポリビニルアルコール水溶液（例、シリカの1/3程度の重量のPVAとなるように）を加え、更に上記と同じ条件で分散を行なうことにより得ることができる。このようにして得られた塗布液は、均一ゾルであり、これを下記の塗布方法により、支持体上に形成することにより、三次元網目構造を有する多孔質層を得ることができる。

【0036】上記多孔質層形成用塗布液の塗布は、例えば、上記塗布液に、所望によりさらに帯電防止剤、媒染剤等を加えて得られた塗布液を、上記支持体（フィルム）上に塗布することにより実施することができる。塗

布は、例えばエクストルージョンダイコーラー、エアードクターコーラー、ブレッドコーラー、ロッドコーラー、ナイフコーラー、スクイズコーラー、リバースロールコーラー、バーコーラー等の公知の塗布方法で行なうことができる。

【0037】多孔質層形成用塗布液の塗布後、その塗布層が減率乾燥速度を示すようになる前に、塗布層上に、本発明の架橋剤を含む溶液を、上記多孔質層形成用塗布液と同様の方法で塗布し、乾燥して、本発明の硬化された色材受容層が得られる。なお、架橋剤溶液はスプレー等の方法で付与してもよい。

【0038】上記塗布層が減率乾燥速度を示すようになる前とは、通常、塗布直後から数分の間であり、この間においては塗布層中の溶剤の含有量が時間に比例して減少する現象である、恒率乾燥速度を示す。このような恒率乾燥速度を示す期間については、化学工学便覧（707～712頁、丸善株式会社発行、昭和55年10月25日）に記載されている。

【0039】本発明の色材受容層は、多孔質層形成用塗布液の塗布後、この塗布層が恒率乾燥速度を示している間に、上記架橋剤含有溶液を塗布またはスプレー等の方法で付与する。多孔質層形成用塗布液の塗布後乾燥は、一般に、5.0～18.0℃で0.5～1.0分間（特に0.5～5分間）行なわれる。この乾燥時間は、当然塗布量により異なるが、上記範囲が適当である。

【0040】多孔質層形成用塗布液の塗布層には、その塗布層が恒率乾燥速度を示す期間内に、架橋剤含有溶液に該塗布層を有する支持体を浸漬することにより、あるいは塗布層に、架橋剤含有溶液をスプレー塗布することにより、該塗布層中に架橋剤を導入あ巣される。架橋剤含有塗布液の塗布は、上記の方法の他、カーテンフローヨー、エクストルージョンダイコーラー、エアードクターコーラー、ブレッドコーラー、ロッドコーラー、ナイフコーラー、スクイズコーラー、リバースロールコーラー、バーコーラー等の公知の塗布方法を利用することができるが、エクストリュージョンダイコーラー、カーテンフローヨー、バーコーラー等を用いて塗布層にコーラーが直接接触しない方法が好ましい。

【0041】架橋剤含有塗布液の色材受容層上の塗布量は、架橋剤換算で0.01～1.0g/m<sup>2</sup>の範囲が一般的であり、0.05～5g/m<sup>2</sup>の範囲が好ましい。架橋剤含有塗布液の塗布後、塗布層は一般に4.0～18.0℃で0.5～3.0分間加熱され、乾燥及び硬化が行なわれる。4.0～15.0℃で1～2.0分間で加熱することが好ましい。例えば、架橋剤として硼酸を使用する場合は、6.0～10.0℃で5～2.0分間加熱することが好ましい。

【0042】次に、本発明の色材受容層の別の形成方法である、無機微粒子及び水溶性樹脂を主成分とする塗布液（多孔質層形成用塗布液）の塗布と同時に架橋剤溶液

を塗布する方法について説明する。多孔質層形成用塗布液と架橋剤含有溶液を、多孔質層形成用塗布液が支持体と接觸するように、支持体上に同時塗布し、硬化させることにより得ることができる。多孔質層形成用塗布液及び架橋剤含有溶液の同時塗布は、例えば、例えはエクストルージョンダイコーラー、カーテンフローコーラーを用いる塗布方法で行なうことができる。同時塗布（重層塗布）後の乾燥は一般に、40～150°Cで0.5～10分間加熱することにより行なわれ、塗布層は硬化される。更に40～100°Cで0.5～5分間加熱することが好ましい。例えば、架橋剤として硼酸を使用する場合は、60～100°Cで5～20分間加熱することが好ましい。

【0043】上記重層塗布を、例えは、エクストルージョンダイコーラーで行なった場合、二種の塗布液はエクストルージョンダイコーラー上で、即ち支持体上に移る前に重層が形成される。そして、二層の塗布層（重層）が支持体に移る際に、すでに二層の界面で架橋反応が起こっているため、エクストルージョンダイコーラーの吐出口付近で吐出塗布液の混合による増粘が発生し易くなり、塗布操作に支障をきたす場合がある。従って、上記同時塗布を行なう際は、多孔質層形成用塗布液及び該架橋剤含有溶液の塗布と共に、さらに架橋剤と反応しない液を、塗布液の層と溶液の層との間に層を介在するように同時三層塗布することが好ましい。架橋剤と反応しない液としては、例えは、架橋剤と反応しない水溶性樹脂（増粘剤として使用）を微量含む水溶液を挙げることができる。

【0044】また、塗布、乾燥後、得られた色材受容層は、例えはスーパーカレンダ、グロスカレンダなどを用い、加熱、加圧下にロールニップ間を通してにより、表面平滑性、透明性及び塗膜強度を向上させることが可能である。しかしながら、このような処理は空隙率を低下させるため（即ちインク吸収性が低下するため）、空隙率の低下が少ない条件を設定して行なう必要がある。

【0045】得られた色材受容層の層厚は、インクジェット記録の場合では、液滴を全て吸収するだけの吸収容

- ①無水シリカ微粒子（平均1次粒子径：7nm；表面シラノール基：2～3個/mm<sup>2</sup>；屈折率：1.45；アエロジル300（日本アエロジル（株）製））
- ②ポリビニルアルコール（鹹化度81.8%；重合度4000；PVA440（クラレ（株）製））
- ③イオン交換水

①のシリカ微粒子を、③のイオン交換水（7.3.3重量部）中に添加して、高速回転湿式コロイドミル（クレアミックス（エム・テクニック（株）製））を用いて、10000rpmの条件で20分間分散させた後、ポリビニルアルコール水溶液（イオン交換水の残り62.7重量部に溶解させたもの）を加えて、更に上記と同じ条件で分散を行なって多孔質層形成用塗布液を得た。

量をもつ必要があり、これは塗膜の空隙率との関連で決定する必要がある。例えはインク量が8nL/mm<sup>2</sup>で、空隙率が60%の場合であれば膜厚が約15μm以上の膜が必要となる。インクジェット記録の場合は、10～50μmの範囲の膜厚が好ましい。感熱転写や電子写真方式の場合は、色材あるいはトナーを表面に吸着することから薄膜で十分であり、0.1～10μmの膜厚が好ましい。

【0046】また、上記色材受容層を主として構成する無機微粒子と水溶性樹脂とは、それぞれ単一素材でも良いし複数の素材の混合系でもよい。また色材受容層は主として上記無機微粒子と水溶性樹脂からなるがそれ以外に粒子の分散性を高める為に各種の無機塩類、PH調整剤として酸アルカリを含んでいてもよい。また塗布適性や表面品質を高める目的で各種の界面活性剤を使用してもよい。表面の摩擦帶電や剥離帶電を抑制する為、あるいは電子写真法に於いて表面電気抵抗を調整する為にイオン導電性を持つ界面活性剤や電子導電性を持つ金属酸化物微粒子を含んでいてもよい。またインクジェット記録に於いて色素を固定し耐水性を高める目的で媒染剤を使用してもよい。また表面の摩擦特性を低減する目的で各種のマット剤を含んでいてもよい。更にまた色材の劣化を抑制する目的で各種の酸化防止剤、紫外線吸収剤を含んでいてもよい。

【0047】また色材受容層と支持体の間に接着性を高めたり、電気抵抗を調整する等の目的で下塗層を設けてもよい。さらに色材受容層は、支持体の片面に設けても良いし、またカール等を抑制する為に、両面に設けても良い。また、OHP等で用いる場合には、色材受容層を片面のみに設ける場合は、その反対面あるいは両面に光透過性を高めるために、反射防止膜を設けても良い。

【0048】

【実施例】

【0049】【実施例1】

(1) 多孔質層（架橋前色材受容層）形成用塗布液の組成（以下の全ての塗布液の配合量を示す重量部の値は、全て固形分又は不揮発分を表わす）

1.0重量部

①無水シリカ微粒子（平均1次粒子径：7nm；表面シラノール基：2～3個/mm<sup>2</sup>；屈折率：1.45；アエロジル300（日本アエロジル（株）製））

3.3重量部

②ポリビニルアルコール（鹹化度81.8%；重合度4000；PVA440（クラレ（株）製））

136.0重量部

【0050】上記塗布液を200μmの厚みの写真印画紙用ラミネート紙の表面に、エクストルージョンダイコーラーを用いて200cc/m<sup>2</sup>の塗布量で塗布し、熱風乾燥機により80°C（風速3m/秒）で3分間乾燥した。塗布層は、この間恒率乾燥速度を示した。この3分間乾燥後、直ちに下記（2）の硼酸含有溶液に、この塗布層を1秒間浸漬させ、80°Cで10分間乾燥した。こ

れにより乾燥膜厚が $27\mu\text{m}$ の色材受容層を形成した。

(2) 硼酸含有溶液

①硼酸	1 重量部
②界面活性剤 (F-144D、大日本インキ化学工業(株)製) 0.2重量部	
③イオン交換水	98.8重量部

【0052】

(3) 第四級アンモニウム塩を有するシランカップリング剤溶液の組成

①M-100C (住友化学工業(株)製)	1.6重量部
②パラトルエンスルホン酸 (10重量%メタノール溶液)	1.6重量部
③シランカップリング剤 (AZ-6160、日本ユニカ(株)製)	4.0重量部
④メタノール	32.8重量部

上記シランカップリング剤溶液を、上記色材受容層上に、#3.1バーコーターを用いて $2.1\text{g/m}^2$ の塗布量(固形分)で塗布し、その後 $80^\circ\text{C}$ で5分間加熱して、第四級アンモニウム塩を有するシランカップリング剤で処理された色材受容層を形成した。上記のようにしてインクジェット用の記録用シートを得た。

【0053】[実施例2] 多孔質層(架橋前色材受容

①乾式シリカ微粒子 (平均1次粒子径: 7nm; 表面シラノール基: 2~3個/nm <sup>2</sup> ; 屈折率: 1.45; アエロジル300 (日本アエロジル(株)製))	10重量部
②ポリビニルアルコール (鹹化度81.8%; 重合度4000; PVA440 (クラレ(株)製))	3.0重量部
③ビニルピロリドン/ジメチルアミノエチル メタクリレート4級塩共重合体 (ルビカットPQ11、ビーエースエフジャパン(株)製)	1.5重量部
④イオン交換水	136.0重量部

【0054】①のシリカ微粒子を、④のイオン交換水(73.3重量部)中に添加して、高速回転湿式コロイドミル(クレアミックス(エム・テクニック(株)製))を用いて、10000rpmの条件で20分間分散させた後、ポリビニルアルコール水溶液(イオン交換水の残り62.7重量部に溶解させたもの)と③の共重合体を加えて、更に上記と同じ条件で分散を行ない、次いでpHを8~9に調整して多孔質層形成用塗布液を得た。

【0055】[比較例1] 実施例1において、(2)の硼酸含有溶液を塗布しなかった以外は同様にしてインクジェット用の記録用シートを作製した。

【0056】[比較例2] 実施例2において、(2)の硼酸含有溶液を塗布しなかった以外は同様にしてインクジェット用の記録用シートを作製した。

【0057】[比較例3] 実施例1において、熱風乾燥機により $80^\circ\text{C}$ (風速3m/秒)で3分間の乾燥を、同温度で4分間乾燥に変えた(塗布層は、この間減率乾燥速度を示した)以外は同様にしてインクジェット用の記録用シートを作製した。

【0058】上記で得られたインクジェット用の記録用シートについて、以下の測定方法によってそのインクジェット適性を評価した。

【0051】

1 重量部
0.2重量部
98.8重量部

層) 形成用塗布液を下記の塗布液を使用した以外は実施例1と同様にして、色材受容層の形成、シランカップリング剤の処理を行なってインクジェット用の記録用シートを得た。

(1) 多孔質層(架橋前色材受容層) 形成用塗布液の組成(以下の全ての塗布液の配合量を示す重量部の値は、全て固形分又は不揮発分を表わす)

30 (1) ヘイズ  
ヘイズメーター(HGM-2DP; スガ試験機(株)製)を用い平行光線透過率を測定し、ヘイズを得た。ただし、各実施例、比較例において、支持体として写真印画紙用ラミネート紙の代わりに厚さ $100\mu\text{m}$ のポリエチレンテレフタレートフィルムを用いて得られた記録用シートを用いて、上記ヘイズを測定した。

【0059】(2) 空隙率  
水銀ポロシメータ(ポアサイザー9320-PC2、(株)島津製作所製)を用いて測定し、分布を得、平均値を計算した。

40 (3) 光沢度  
得られた記録シートについて、JIS-P-8142(紙及び板紙の75度鏡面光沢度試験方法)に記載の方法に従って、光沢度を測定した。

【0060】(4) インク吸収速度  
インクジェットプリンター(PM-700C; セイコーエプソン(株)製)により、記録用シートへのY(黄)、M(マゼンタ)、C(シアン)、K(黒)、B(青)、G(緑)及びR(赤)のベタ印字し、その後(約10秒後)に紙を接触押圧し、インクの紙への転写の有無で下記のように判定した。

50 AA: 紙にインキが転写されなかった。

CC：紙にインキが転写された。

(5) ヒビ割れの発生

得られた記録用シートを目視で観察し、表面に発生したヒビ割れの有無、及びその大きさに従い、下記のように評価した。

AA：ヒビ割れが見られない

BB：1～2mmの長さのヒビ割れが見られる

CC：3mm以上の長さのヒビ割れが見られる

上記評価の結果を下記の表1に示す。

【0061】

【表1】

表1

	ヘイズ (%)	空隙率 (%)	光沢度 (%)	インク 吸収速度	ヒビ割れ
実施例1	13.3	62	53	AA	AA
実施例2	14.0	60	55	AA	AA
比較例1	16.0	61	53	AA	BB
比較例2	17.0	60	54	AA	CC
比較例3	13.8	62	53	AA	BB

【0062】

【発明の効果】本発明の記録用シートは、インクジェット記録においては液状インクを早く吸収し、インク滲みやインク溜まりの無い精細な画像が得ができるのみならず、多孔質層である色材受容層をヒビ割れの発生を起こすことなく、高画質の画像を簡易に形成すること

ができる。また、本発明の記録シートの吸収性、滲み防止に優れていることから、熱転写記録や電子写真記録の各種記録方式においても色材あるいはトナーの接着性が向上する。従って、本発明の記録用シートは、種々の記録方法に適し、かつ生産性に優れた記録用シートであることができる。